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PROPERTIES OF
HIGH EMITTANCE MATERIALS

by R. E. Cleary, R. Emanuelson, W. Luoma, and C. Ammann

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FOREWORD

This report describes the research activity carried out in fulfillment of Contract NAS 3-4174. The work was performed during the period from May 14, 1964, through May 30, 1968. It was conducted under the direction of the Space Power Systems Division, NASA-Lewis Research Center with R. L. Davies and J. A. Milko as Project Managers.

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SUMMARY

A four-year program was conducted to determine the suitability of selected high-emittance materials for use as coatings on beryllium, columbium-1 percent zirconium, and AISI-310 stainless steel when these materials are used in space powerplant radiators.

The coated beryllium specimens were aged in vacuum at 800°F, 1200°F, and 1400°F for periods up to 1000 hours. The effects of the aging process on the stability and emittance of the coatings were determined. The materials coated on beryllium included calcium titanate, iron titanate, zirconium titanate, anodized beryllium, and aluminum oxide aluminum titanate. The first three of these were found to be compatible with beryllium for at least 1000 hours at temperatures up to 1200°F, although the zirconium titanate appeared to form a weaker bond with the beryllium than did the other coating materials. Coatings of anodized beryllium and aluminum oxide aluminum titanate were found to be unsuitable for use as high emittance coatings on beryllium. The emittance of the iron titanate and zirconium titanate coatings remained relatively constant during the aging process at 0.91 at 900°F. The emittance of the calcium titanate coating was increased permanently by aging from 0.68 to 0.92. Aging at 1400°F resulted in vaporization of the beryllium. Aging at 1200°F or below produced no changes to the beryllium other than an insignificant, but detectable, diffusion of the coating constituents across the coating-substrate boundary and an almost negligible decrease in weight.

Four coated specimens were selected for long-term emittance testing on the basis of preliminary screening tests. These were calcium-titanate-coated AISI-310 stainless steel, iron-titanate-coated AISI-310 stainless steel, iron-titanate-coated columbium-1 percent zirconium, and columbium-1 percent zirconium coated with aluminum oxide aluminum titanate. The coated AISI-310 stainless steel specimens were heated in vacuum to 1350°F for 20,000 hours, and the columbium-1 percent zirconium specimens were heated in vacuum to 1700°F for 10,000 hours. All specimens were thermally cycled to room temperature once each week.

The calcium-titanate-coated AISI-310 stainless-steel specimen demonstrated a stable emittance of about 0.89, and the coating remained well bonded to the substrate. Only a very slight amount of interaction occurred between the coating and the substrate.

The iron-titanate-coated AISI-310 stainless-steel specimen demonstrated a stable emittance of about 0.88. Some changes in the structure of the coating occurred, but they had no observable effect on the emittance of the specimen. In addition, coating separation occurred at the ends of the specimen and in small areas around the black-body holes. Very limited interaction between the coating and the substrate occurred.

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Both of the AISI-310 stainless-steel substrates were harder after testing than before testing. This is attributed to the formation of sigma phase and finely divided carbide precipitates.

The iron-titanate-coated columbium-1 percent zirconium specimen initially had an emittance of 0.88, but it decreased to 0.85 between 600 hours and 1800 hours of testing at 1700°F. By the end of the test at 10,000 hours, the emittance was 0.84. The test produced no visible changes in the coating other than a slight darkening in color. No spalling or cracking of the coating could be seen. Considerable oxygen was picked up by the columbium-1 percent zirconium, however, and iron diffused into the substrate.

The aluminum oxide aluminum titanate coating applied to columbium-1 percent zirconium deteriorated during testing. The emittance was initially 0.87, but it decreased to 0.80 by the end of the test (10,500 hours), and post-test analysis of the coating indicated that substantial chemical and structural changes had occurred. Initially, the aluminum titanate was broken down to Al_2O_3 and TiO_2. Some of the Al_2O_3 was subsequently reduced to aluminum, which then reacted with the columbium to form $CbAl_3$, and some of the TiO_2 was reduced to Ti_2O_3. In addition, some of the columbium was oxidized to CbO_2.

A limited amount of diffusion of coating constituents into the columbium-1 percent zirconium occurred in both specimens. In the aluminum-oxide-aluminum-titanate-coated specimen, the columbium-1 percent zirconium substrate picked up approximately 1500 ppm aluminum, with most of the aluminum being concentrated in the region within 1 mil of the coating-substrate interface. Approximately 120 ppm of titanium was also picked up by the substrate. This material was also concentrated within 1 mil of the coating-substrate interface. In the iron-titanate-coated specimen, the columbium-1 percent zirconium substrate picked up approximately 2000 ppm of iron in the outer 4 mils of the substrate wall. Approximately 140 ppm of titanium was found in the outer 1 mil of the substrate wall. The oxygen picked up by the substrate during this test amounted to approximately 3000 ppm. The elements which diffused into the substrates tended to increase the hardness of the substrate above the level expected for fully annealed columbium-1 percent zirconium, but the exact mechanisms involved have not been clearly defined.

Two columbium-1 percent zirconium tubes coated with iron titanate were thermally cycled in vacuums of 1 x 10^{-7} torr or better. One of these was cycled between 1500°F and 1800°F for 5,000 hours, and the other was cycled between 1500°F and 1900°F for 10,000 hours. The specimen cycled between 1500°F and 1800°F demonstrated a stable emittance of about 0.88 throughout the test. The coating remained well bonded to the substrate, but the coating structure was changed from iron titanate to a mixture of iron titanate and ti-

tanium oxide. The specimen cycled between 1500°F and 1900°F for 10,000 hours demonstrated an initial emittance of about 0.89, but the emittance decreased to about 0.77 at the end of the test, apparently as a result of separation of the coating from the substrate. The crystalline structure of the coating after testing differed from that of the coating before testing, but it was not possible to identify all of the crystalline structures present. Analysis of the substrates of these specimens revealed that essentially the same changes occurred during testing as in the previously tested specimens with columbium-1 percent zironium substrates. In the 5,000-hour test, approximately 3900 ppm of oxygen were picked up, with iron diffusion to a depth of 4 mils and titanium diffusion to a depth of about 0.5 mil beneath the coating-substrate interface. In the 10,000-hour test, approximately 5200 ppm of oxygen were picked up. Iron diffused to a depth of about 7 mils, and titanium diffused to a depth between 4 and 5 mils.

I. INTRODUCTION

A. SCOPE

A four-year program was conducted to determine the suitability of selected
high-emittance materials for use as coatings on space powerplant radiators.
The coatings were evaluated at elevated temperatures in air and in vacuum
with respect to emittance stability, adherence, and compatibility when applied
to AISI-310 stainless steel, columbium-1 percent zirconium, and beryllium
substrates.

The work was divided into three phases. The first phase involved the evalua-
tion of selected materials coated on beryllium and aged at 800°F and 1200°F
for periods up to 1000 hours, and the second phase involved the evaluation of
selected coatings on columbium-1 percent zirconium and AISI-310 stainless
steel for periods up to 20,000 hours. Both of these phases were directed toward
evaluating coatings for use in advanced Rankine and thermionic systems. The
third phase consisted of two thermal cycling endurance tests on iron-titanate-
coated columbium-1 percent zirconium specimens. One of these specimens
was cycled between 1500°F and 1800°F for 5,000 hours in vacuum, and the other
was cycled between 1500°F and 1900°F for 10,000 hours in vacuum. These tests
were designed to evaluate the suitability of iron titanate as a coating for Brayton-
cycle solar heat receivers.

All of the experimental and analytical work described in this report was per-
formed directly by Pratt & Whitney Aircraft except where other organizations
are specifically referenced.

B. EMITTANCE MEASUREMENT AND ERROR ANALYSIS

Emittance measurements were made on two types of specimens, and two different
techniques were used. Most of the specimens tested during the program were
coated nine-inch long tubes one-quarter inch in diameter with a wall thickness of
0.010 inch. These specimens were electrically resistance heated, and tempera-
tures were measured with thermocouples and with an optical pyrometer focused
on one of two small black-body holes drilled into the specimen. With the specimen
in a vacuum chamber supported in a manner that prevents appreciable heat con-
duction from the specimen test section, all of the electrical energy supplied to the
specimen test section is radiated. Since the chamber walls were blackened and
the specimen surface area was considerably smaller than the inside surface of the
chamber, the net power radiated, as given by the Stefan-Boltzmann equation,
could be equated to the electrical power supplied to the specimen. This equation
was then solved for emittance:

$$\epsilon_{th} = \frac{IV}{\sigma A(T_s^4 - T_o^4)}$$

where:

ϵ_{th} = Total hemispherical emittance

I = Current through the test section

V = Voltage drop across the test section

σ = Stefan-Boltzmann constant

A = Surface area of the test section radiating power IV

T_s = Temperature of the test section

T_o = Temperature of the chamber wall

With the equipment used, the electrical currents and voltages could be measured to within 0.2 percent, the test section radiating area could be measured to within 0.25 percent, and temperatures could be measured to within 0.5 percent with thermocouples or 0.4 percent with an optical pyrometer. Since errors from other sources were negligible, the maximum errors in the reported total hemispherical emittance values determined by this method are ±2.7 percent when temperatures were measured by thermocouples and ±2.3 percent when temperatures were measured by an optical pyrometer. Early in the program, the validity of using optical pyrometer temperatures for calculating the emittance was questioned since the optical pyrometer temperatures are actually the temperatures of the inside of the tube whereas the equation is strictly correct only when the temperature of the outer surface of the tube is used. An analysis was performed to determine the difference between the two temperatures. The analysis indicated that the maximum temperature difference occurring with the materials and temperatures used during this program would be 0.6°F. This represents an error of less than 0.03 percent, and, therefore, may be neglected.

The coated beryllium specimens used for emittance measurement were in the form of flat strips nine inches long, 0.4 inch wide, and 0.010 inch thick or in the form of flat plates which were three inches square and 0.100 inch thick. The geometry of these specimens was not appropriate for electrical resistance heating, and, therefore, a thermionic method was used. Thermionic heating was achieved by generating an electron beam from thoriated filaments heated to approximately 3000°F. With this method, it was not possible to measure the heating power supplied to the specimens accurately. Consequently, the emittance was determined by a thermal decay method. For this method, the specimen is heated to a particular temperature and then allowed to cool. The rate of cooling is measured, and the cooling rate data is used to calculate the rate at which heat is radiated. The rate at which heat is radiated is given by:

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$$\text{heat radiated} = -MC \cdot \frac{dT}{dt}$$

where:

M = Mass of the specimen
C = Specimen heat capacity
$\dfrac{dT}{dt}$ = Specimen cooling rate

Since the test conditions were the same as for the tubular specimens, the Stefan-Boltzmann equation could be applied in the form:

$$\epsilon_{th} = \frac{MC \,(dT/dt)}{\sigma\, A(T_s^4 - T_o^4)}$$

This equation is valid for specimens coated on all surfaces providing the convective and conductive energy losses are negligible. However, some of the specimens were coated on only one side. For these specimens, the equation was modified as follows:

$$\epsilon_{th} = -\frac{MC(dT/dt)}{\sigma\, A_1(T_s^4 - T_o^4)} - \frac{A_2\, \epsilon_2}{A_1}$$

where:

A_1 = Area of the coated portion of the specimen

ϵ_2 = Emittance of the uncoated portion of the specimen

A_2 = Area of the uncoated portion of the specimen

The value of the emittance used for the uncoated portion of the specimen was determined experimentally and was not equal to the actual value for uncoated beryllium. At the temperature at which the filaments were operated for thermionic heating, some vaporization of the thorium occurred, and the thorium subsequently condensed on the uncoated surface of the specimen. The emittance of the lightly plated beryllium surface was found to vary from 0.16 at 500°F to 0.22 at 1000°F. The corresponding values for polished beryllium are 0.15 at 500°F and 0.18 at 1000°F.

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II. BERYLLIUM STUDIES

A. INTRODUCTION

The beryllium studies involved the aging of a number of coated beryllium plates in vacuum for periods of 100, 500, and 1000 hours at temperatures of 800°F, 1200°F, and 1400°F, followed by emittance testing to determine the effect of the aging process on the emittance properties. Initially, aging was to be conducted at 800°F and 1400°F, but early testing at 1400°F in vacuums of 1×10^{-7} torr or better resulted in vaporization of the beryllium. Consequently, the maximum temperature for later tests was lowered to 1200°F by a directive from NASA. The specimens were aged in groups of three to determine the reproducibility of the data.

One specimen from each group was examined for metallurgical properties after aging. The coatings were analyzed by X-ray diffraction and spectrographic analysis, and the substrates were examined for microhardness and microstructure. In addition, electron-beam microprobe analyses were performed on one specimen from each group that was aged at 1200°F for 1000 hours. The analyses were performed by the Advanced Metals Research Corporation, Burlington, Massachusetts and by the United Aircraft Research Laboratory using a Norelco analyzer.

Microhardness measurements were made for specimens from each group in accordance with the contract requirements, but it was not possible to provide a meaningful correlation between hardness and depth below the surface. The reason for this is the anisotropic properties of the beryllium crystal.[1] Diamond pyramid hardness values varied by as much as 262 kg/mm^2 in adjacent areas (with a representative value of 190 kg/mm^2), presumably because the measurements were made on different crystals. With this large a difference being produced by crystal orientation, any small changes in overall hardness with depth were completely undetectable, since the effects of impurities or aging and those of orientation were inseparable. Consequently, it was deemed inappropriate to tabulate the hardness values obtained together with the depths at which the measurements were made. Such a tabulation might, in some cases, appear to indicate a trend which, in fact, has no justifiable basis.

B. BERYLLIUM ANALYSIS

The beryllium plates used for the aging specimens were procured from the Beryllium Corporation of America in the form of three-inch by three-inch plates which were 0.10 inch thick. The material was designated as high purity IS-2

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[1] Raised numbers refer to references listed at the end of this document.

ingot sheet. Spectrographic analysis of the material, as received, revealed the presence of 0.06 percent silicon, 0.05 percent iron, 0.02 percent nickel, 0.01 percent titanium, 0.01 percent manganese, and traces of chromium, copper, magnesium, lead, gold, and tin. Chemical analysis showed 0.8 percent beryllium oxide to be present

The plates were received in two shipments, each from different heats, and the microstructures of the material differed significantly between shipments. As shown in Figure 1, the material received in the first shipment was characterized by elongated grains, whereas the material received in the second shipment consisted of equi-axed, recrystallized grains. The white streak in the photomicrograph at the coating-substrate interface was produced by coating material removal during specimen preparation. Cross-hatch lines in the substrate materials are indicative of twinning caused by cold working.

C. COATING SELECTION AND SPECIMEN PREPARATION

Five coatings were selected for testing on the basis of emittance test results from other programs and on the basis of a literature search. Iron titanate and calcium titanate were selected on the basis of high emittance values and good bond strength demonstrated during 10,000-hour tests on other metal substrates. Zirconium titanate had been tested previously at 1700°F as a coating on columbium-1 percent zirconium. The coating did not exhibit adequate emittance stability at 1700°F for long-term testing, but the emittance at temperatures below 1700°F was about 0.88, so the material appeared to be promising for use at lower temperatures. A short-term endurance test of a zirconium-titanate-coated columbium-1 percent zirconium tube was conducted at 1200°F for 290 hours, and the emittance remained steady at 0.88 throughout the test. Consequently, the material appeared suitable for testing on beryllium. Two materials were tested which had not been tested previously at Pratt & Whitney Aircraft. These were anodized beryllium and aluminum oxide-aluminum titanate.

All of the coatings were applied by plasma spraying except, of course, for the anodized beryllium. The plasma-spray parameters used are listed in Appendix A.

D. TEST APPARATUS AND PROCEDURES

Two furnaces were constructed for aging the specimens. Each is a general purpose box-type bench furnace capable of maintaining temperatures up to 2300°F (see Figure 2). Provisions were made for installing a hot-wall vacuum chamber 6 inches in diameter and 22 inches long. Three thermocouples were mounted along the length of the chamber exterior to monitor the furnace temperature. The specimens were mounted in a stainless-steel sample holder specially constructed for the purpose. Four Chromel-Alumel thermocouples were welded to the sample

First Shipment   200X
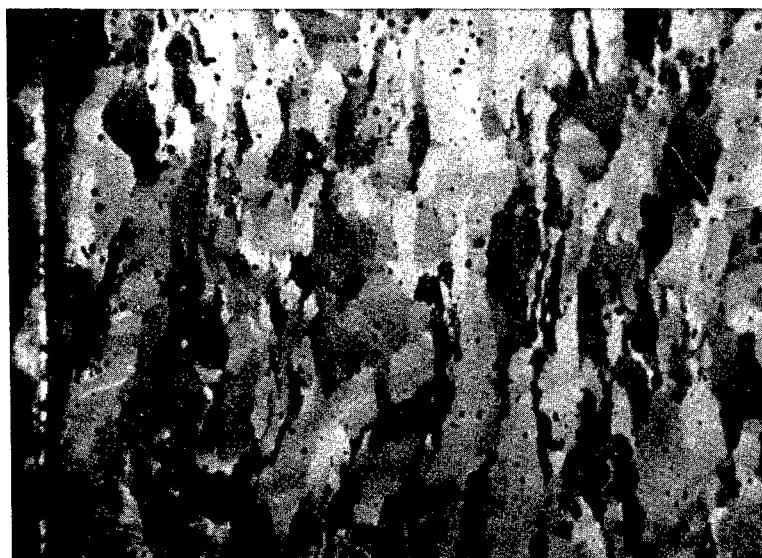
First Shipment   50X

Etchant: 49% NH_2SO_3H, 16% $H_2C_2O_4$, 1% HF, 34% H_2O

Figure 1   Typical Cross Sectional Photomicrographs
of Beryllium Plates from First and
Second Shipments

Second Shipment   200X
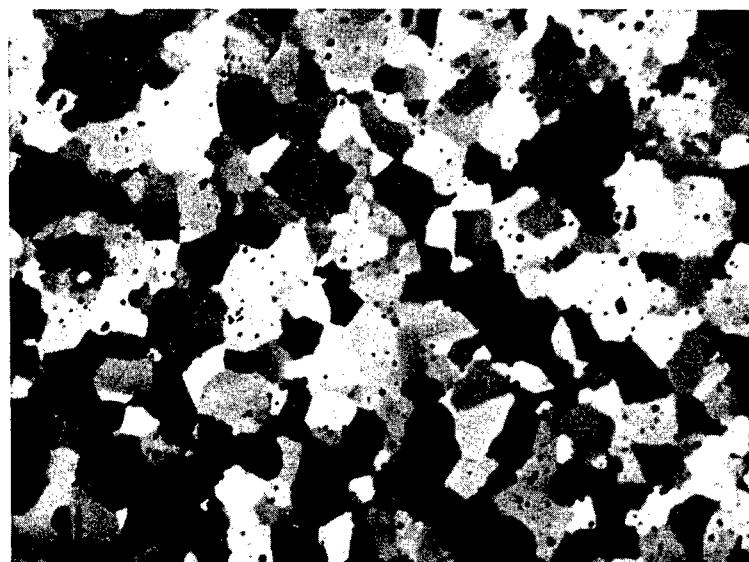
Second Shipment   50X

Figure 1   Concluded
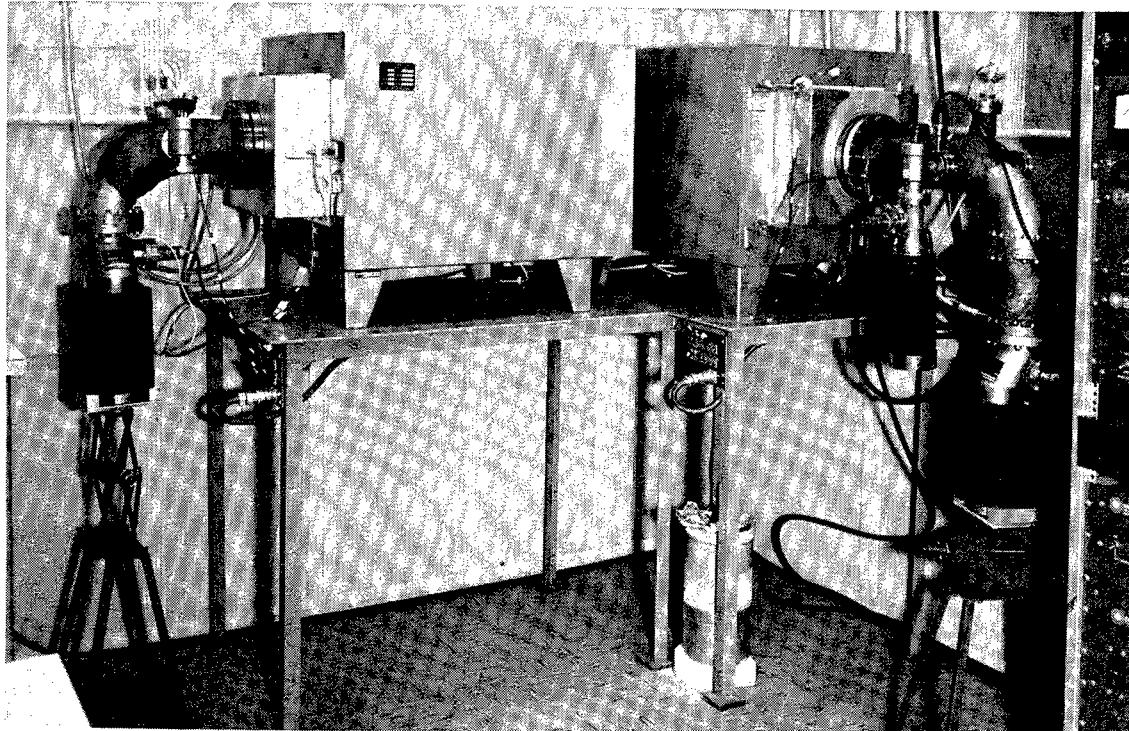
Figure 2   Vacuum Aging Furnaces Used for Beryllium Studies

holder to provide the temperature profile of the test area. A titanium sublima-
tion pump was constructed for use with either furnace assembly to provide a
larger pumping speed than is available with an ion gettering pump. All basic
furnace controls and instrumentation read-out units were grouped in a console.
Included were temperature controllers for the furnaces, power supplies for the
ion gettering pumps, an ionization gage control unit, a thermocouple gage con-
trol unit for use during bakeout, a switching arrangement and a slidewire milli-
volt potentiometer for the thermocouple output measurement, and the control
unit for the titanium sublimation pump. The console is shown in Figure 3.
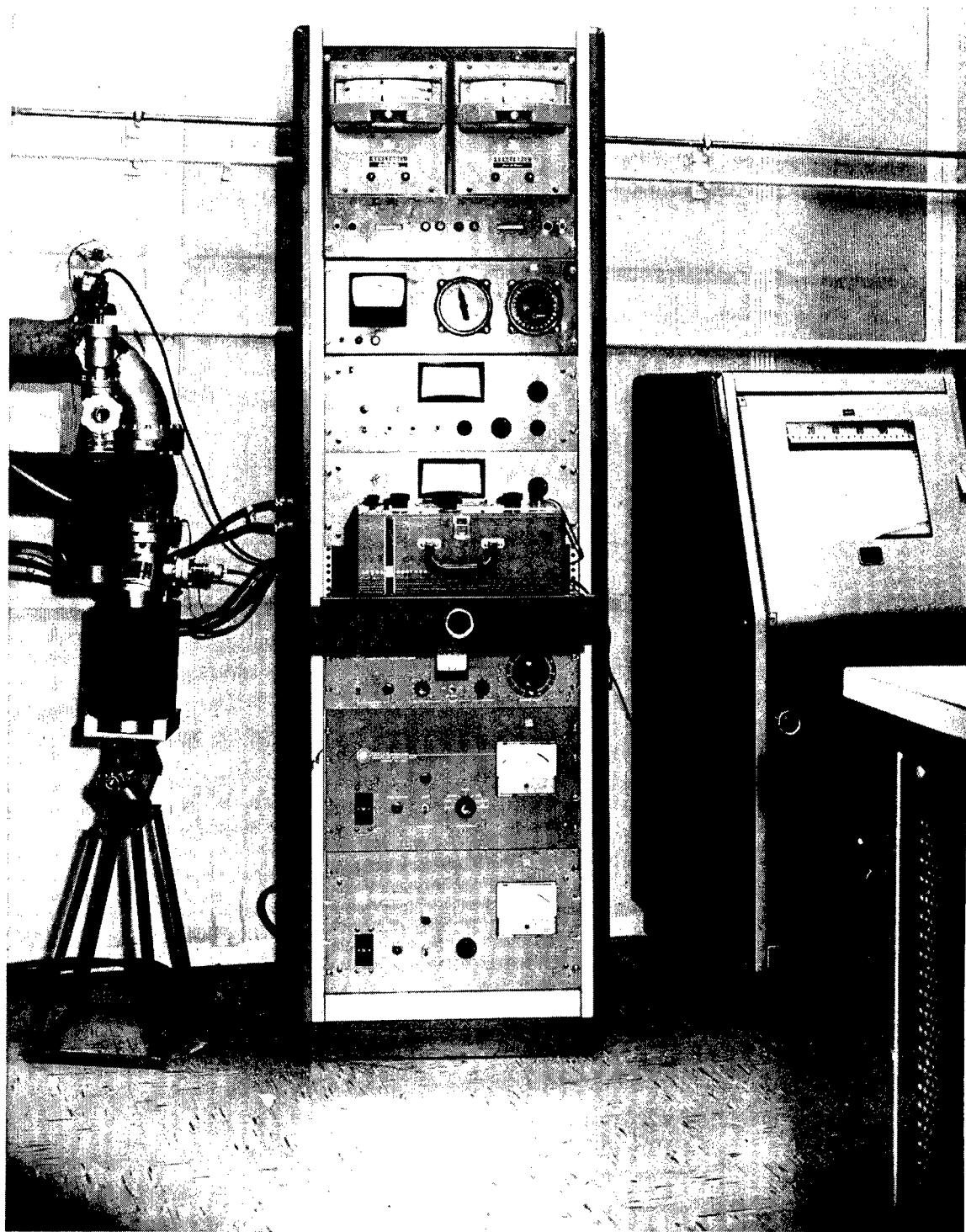
Figure 3   Control Console for Beryllium Aging Studies

Emittance measurements were made in the thermal decay apparatus shown in Figure 4. This equipment includes a vacuum chamber, an evacuation system, an instrumentation flange, specimen heaters, and temperature measurement instrumentation. The specimen was housed in an 8-inch diameter, 16-inch long cylindrical chamber with convoluted walls. The interior of the chamber was painted with Krylon flat black paint. The combination of high emittance paint and irregular walls resulted in a heat sink with an emittance closely approaching unity. The test chamber was mounted on a multiport vacuum base plate with provisions for feedthroughs for high voltage leads, thermocouple leads, and coolant flow. The base plate was manufactured by Varian Associates. The chamber was enclosed by a Pyrex bell jar, and the system was evacuated to 1 x 10^{-5} torr or less by a Veeco VS-400 pumping station. Specimen temperatures were recorded by a Bristol Dynamaster strip chart recorded, and sink temperatures were measured with a Leeds and Northup 8686 potentiometer. The specimens were heated by a Sel Model 135 electron-beam power supply which generated on electron beam between thoriated tungsten filaments and the uncoated surface of the specimen.
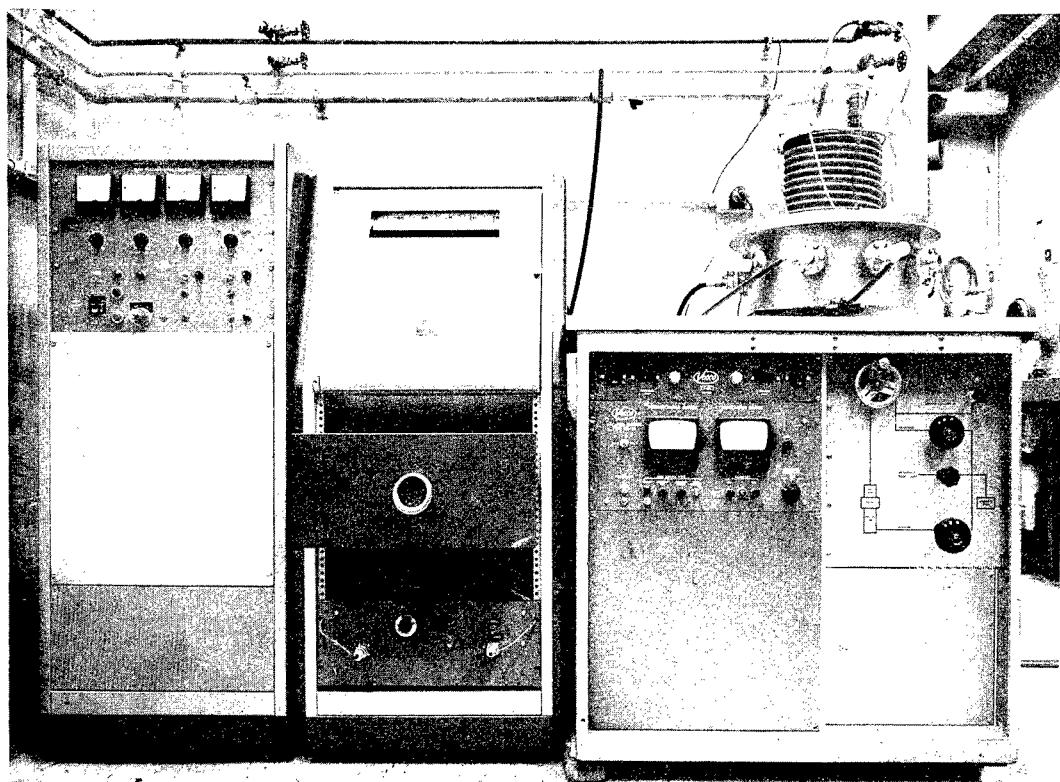
Figure 4   Thermal Decay Apparatus for Emittance Measurement   X-21989

For emittance measurement, the specimen was initially heated to 1100°F by the electron beam. The beam was generated by heating the filaments to approximately 3000°F and applying a negative potential of 5000 volts to the filaments relative to the specimen. The resulting beam current of approximately 100 milliamperes heated the specimen to the required temperature in approximately 10 minutes. When the starting temperature was reached, the electron beam was shut off, the sink temperature was measured, and the strip chart recorder started. Testing was concluded when the specimen reached 400°F. Throughout the test, the sink temperature was maintained at a constant level by coolant which circulated continuously through the chamber.

E. TEST RESULTS

1. Calcium-Titanate Coating on Beryllium

a. Material Description

The calcium titanate used for these specimens was obtained from the Titanium Division of the National Lead Corporation. The X-ray diffraction analysis performed before the material was used detected only $CaTiO_3$ to be present. The emission spectrographic analysis showed the only other elements present to be traces of silicon and magnesium. The particle size distribution for the powder as determined by screen analysis is shown in Table I

TABLE I

PARTICLE SIZE DISTRIBUTION OF CALCIUM
TITANATE USED FOR BERYLLIUM STUDIES

Particle Size (Microns)	Cumulative Weight Percent
66	23.0
52	58.0
41	80.0
33	81.0
26	87.0
21	93.0
17	96.5
15	96.7
13	97.0
10	98.6
8	99.0
6	100.0

b. Aging Tests

Calcium-titanate-coated beryllium plates were aged at 800°F for 100, 500, and 1000 hours, at 1400°F for 100 hours, and at 1200°F for 500 and 1000 hours. After being aged at 800°F, the specimens exhibited no changes in appearance other than a slight darkening of the coating. No cracking, spalling, or indication of bond deterioration occurred.

Aging for 100 hours at 1400°F in a vacuum of 1×10^{-8} torr resulted in a considerable darkening of the coating, although the texture was unchanged, and no cracking or spalling of the coating was observed. However, spectrographic analysis of the coating detected the presence of beryllium, and X-ray diffraction analysis detected the probable present of beryllium oxide. Since the aging conditions were known to be marginal with respect to the vapor pressure of beryllium, and since it appeared that vaporization had, in fact, occurred, it was decided that the maximum aging temperature should be lowered to 1200°F.

Subsequently, two additional groups of specimens were aged at 1200°F, one for 500 hours and the other for 1000 hours. As shown in Figure 5, the specimens were darker after aging than before, with the color change being greater for the specimens aged for the longer period. However, the color change for these specimens was always less than that for the specimens aged at 1400°F. No spalling, cracking, or change in texture occurred.

| UNAGED | AGED 100 HOURS 1400°F | AGED 500 HOURS 1200°F | AGED 1000 HOURS 1200°F |
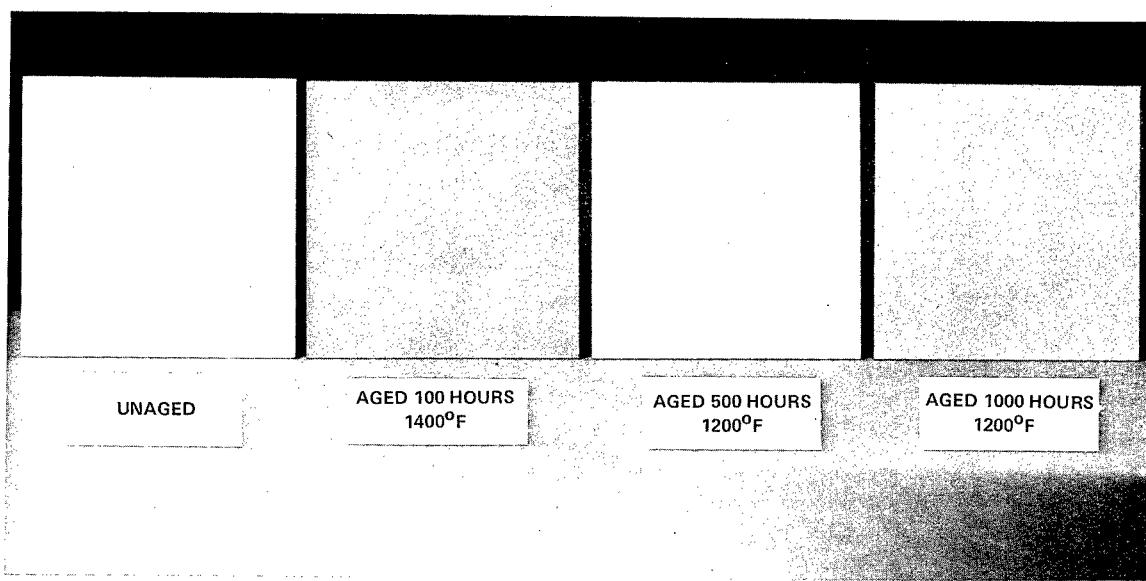
Mag: 0.45X

Figure 5   Appearance of Calcium-Titanate-Coated Beryllium Plates Before Aging and After Aging at 1400°F for 100 Hours, at 1200°F for 500 Hours, and at 1200°F for 1000 Hours

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All of the specimens were weighed before and after aging, and the results are shown in Table II. As shown, the weight change of all specimens except those aged at 1400°F was very small. Because the weight changes were almost insignificant, no attempt was made to determine causes for the variations observed. The specimens aged at 1400°F lost approximately 0.025 gram. A considerable portion of this loss is attributable to the beryllium lost through vaporization.

TABLE II

WEIGHTS OF CALCIUM-TITANATE-COATED BERYLLIUM
SPECIMENS BEFORE AND AFTER AGING

Specimen	Test Temperature (°F)	Test Hours	Weight (gm)		Percent Change in Weight	Average Percent Change in Weight	Gross Change in Weight (mg/yr)
			Before Test	After Test			
1	800	100	30.482	30.481	0		
2	800	100	30.493	30.489	0.01	0.01	876
3	800	100	30.980	30.978	0.01		
4	800	500	29.744	29.740	0.01		
5	800	500	30.008	30.004	0.01	0.01	175
6	800	500	29.816	29.810	0.02		
7	800	1000	29.825	29.816	0.03		
8	800	1000	29.896	29.886	0.03	0.03	264
9	800	1000	29.828	29.819	0.03		
10	1400	100	30.386	30.361	0.08		
11	1400	100	30.498	30.476	0.07	0.08	7008
12	1400	100	30.366	30.340	0.09		
13	1200	500	30.428	30.420	0.03		
14	1200	500	30.410	30.399	0.04	0.05	875
15	1200	500	29.884	29.859	0.08		
16	1200	1000	30.638	30.628	0.03		
17	1200	1000	30.549	30.542	0.02	0.03	264
18	1200	1000	30.540	30.532	0.03		

Note: Specimen size is 3 inches square and 0.10 inch thick

One specimen from each group was examined for metallurgical, chemical, and mechanical properties. The results of the spectrographic analyses are presented in Table III. As shown, with the exception of the specimens aged at 1400°F, no significant changes occurred in the impurities present.

TABLE III

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF CALCIUM TITANATE APPLIED
TO BERYLLIUM

	Impurity Content (Weight Percent)								
	Al	Be	Cr	Cu	Fe	Mg	Mn	Ni	Si
As Sprayed	trace	0	0	0.01	trace	trace	trace	trace	0.02
1000 Hours at 800°F	trace	0	0	trace	trace	0.01	trace	0	0.01
100 Hours at 1400°F	trace	trace	0	trace	trace	trace	trace	0	trace
500 Hours at 1200°F	trace	0	0.02	0	trace	trace	trace	0	trace
1000 Hours at 1200°F	0.01	0	0	0	trace	trace	trace	0	trace

X-ray diffraction tests detected $CaTiO_3$ as the only phase present in all coatings except those aged at 1400°F. Traces of BeO were detected in the coatings aged at 1400°F. The BeO is attributed to the vaporization of the beryllium followed by oxidation to BeO on exposure to air.

Photomicrographs were taken of one specimen from each test. The microstructure of all specimens remained unchanged as a result of aging, except for those aged at 1400°F. These specimens exhibited some annealing, as expected. Typical photomicrographs of specimens aged for 1000 hours at 800°F and 1200°F are shown in Figure 6. The beryllium for these specimens was received in the first shipment and exhibits the elongated structure characteristic of that shipment.
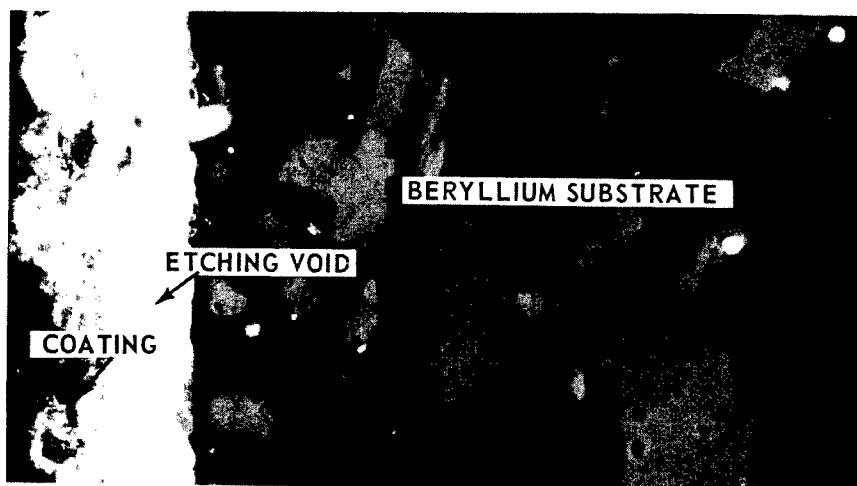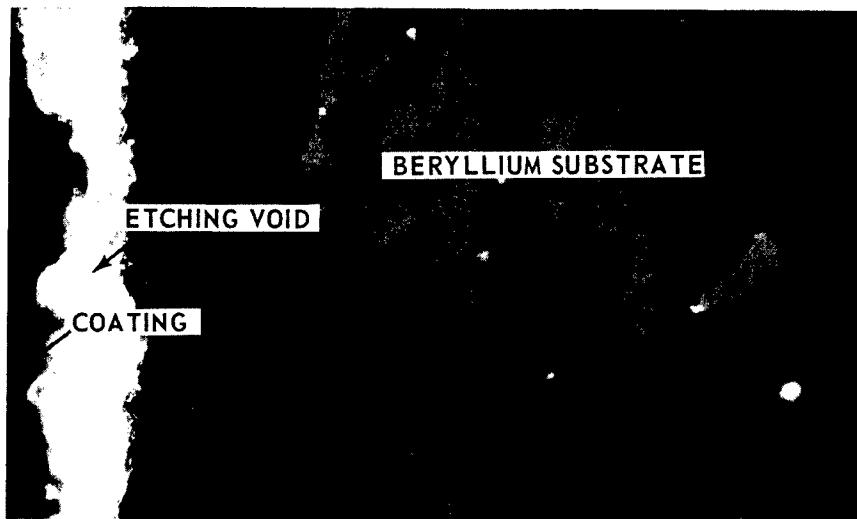
Etchant: 49% NH_2SO_3H, 16% $H_2C_2O_4$, 1% HF, 34% H_2O Mag: 200X

Figure 6   Typical Cross Sectional Photomicrographs of Calcium-Titanate-
Coated Beryllium Plates Aged for 1000 Hours at 800°F (Top) and
1200°F (Bottom)

An electron-beam microprobe analysis was performed on the cross section of
one of the specimens aged at 1200°F for 1000 hours and on a specimen which was
not aged. The electron-beam traverse over the cross section was made at an
angle of 45 degrees to the substrate-coating interface to a depth of 3 mils. The
distributions of calcium and titanium were determined. As shown in Table IV,
only a slight amount of diffusion of calcium and titanium into the beryllium was
detected. Oxygen concentrations were too low to measure in either of the speci-
mens. Although the concentrations of calcium and titanium are higher for the
aged specimen than for the unaged specimen, the total amounts are extremely
small on an absolute scale and represent a level of diffusion which, in all pro-
bability, is not detrimental to the material properties.

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TABLE IV

CONCENTRATIONS OF CALCIUM AND TITANIUM ACROSS BERYLLIUM PLATES COATED WITH CALCIUM TITANATE

As Sprayed			After Aging 1000 Hours at 1200°F		
Depth Below Interface (Mils)	Concentration (Weight Percent)		Depth Below Interface (Mils)	Concentration (Weight Percent)	
	Calcium	Titanium		Calcium	Titanium
0	0.02	0.01	0	0.03	0.01
0.07	0.01	0.01	0.07	0.02	0
0.14	0.01	0.01	0.14	0.02	0.01
0.21	0.01	0	0.21	0.01	0.01
0.28	0.01	0.01	0.28	0.01	0.01
0.35	0.01	0	0.35	0.01	0.01
0.42	0.01	0	0.42	0.01	0
0.50	0	0	0.49	0.01	0.01
0.57	0	0	0.57	0	0
0.64	0.01	0	0.64	0	0
0.71	0	0	0.71	0	0
0.78	0	0	0.78	0	0
0.85	0	0	0.85	0	0
0.92	0	0	0.99	0	0
1.0	0	0	1.1	0	0
1.1	0	0	1.3	0	0
1.3	0	0	1.4	0	0
1.4	0	0	1.6	0	0
1.6	0	0	1.7	0	0
1.7	0	0	1.8	0	0
2.0	0	0	2.0	0	0
2.4	0	0	2.3	0	0
2.8	0	0	2.7	0	0
3.1	0	0	3.0	0	0

Note: Minimum detectable concentrations of calcium and titanium are 0.01 weight percent. Concentrations below this level are reported as 0.

c. Emittance Tests

A beryllium strip coated with a 4-mil-thick layer of calcium titanate was tested for emittance at 1200°F for 626 hours. The strip form of this specimen permitted the emittance to be determined at steady-state conditions using electrical resistance heating. Initially, the emittance was about 0.88, but, after 100 hours, the emittance began to decrease, reaching a final value of 0.78. Examination of the specimen after testing revealed that coating separation had occurred, causing the emittance to decrease.

Additional tests were conducted on unaged and aged coated plates in the thermal decay apparatus. The emittance of the unaged specimen ranged between 0.73 at 400°F and 0.68 at 1000°F as shown in Figure 7. Subsequently, the emittance of a specimen which had been aged at 1200°F for 1000 hours was measured, and the emittance was found to range between 0.89 at 400°F and 0.92 at 900°F. The increase in emittance produced by aging was expected since previous short-term endurance tests of calcium-titanate-coated stainless steel had shown similar trends. The process is similar to a curing process, since the coating maintains the higher emittance level once it is attained.

To explore the curing phenomenon further, the unaged specimen was installed in the thermal decay test equipment and aged at a temperature of approximately 1000°F, with emittance measurements being made at intervals during the process. The emittance values obtained at 900°F are plotted in Figure 8. As shown, the emittance increased from the 0.68 value obtained previously to 0.95 after 135 minutes of aging. The fact that the final value was higher than that obtained from the specimen aged at 1200°F for 1000 hours is indicative of additional amounts of thorium on the uncoated specimen surface from the thoriated-tungsten filament used in the thermal decay apparatus. The deposition raised the emittance of the uncoated surface above the value assumed in the calculations. Consequently, the calculated value of the emittance for the coated surface is slightly higher than the true value.

2. Iron-Titanate Coating on Beryllium

a. Material Description

The iron titanate powder used was obtained from the Continental Coatings Corporation, Cleveland, Ohio, and was designated FCT-11. X-ray diffraction analysis detected the presence of no crystalline phases other than Fe_2TiO_5. Spectrographic analysis detected the presence of 0.6 percent manganese, 0.4 percent silicon, 0.5 percent aluminum, and 0.3 percent magnesium. The particle size distribution for the powder as determined by screen analysis is shown in Table V.

BEFORE AGING

TEMPERATURE ~ °F

EMITTANCE AT 900°F

AGING TIME AT 1000°F ~ MINUTES

AFTER AGING 1000 HOURS AT 1200°F

TEMPERATURE ~ °F
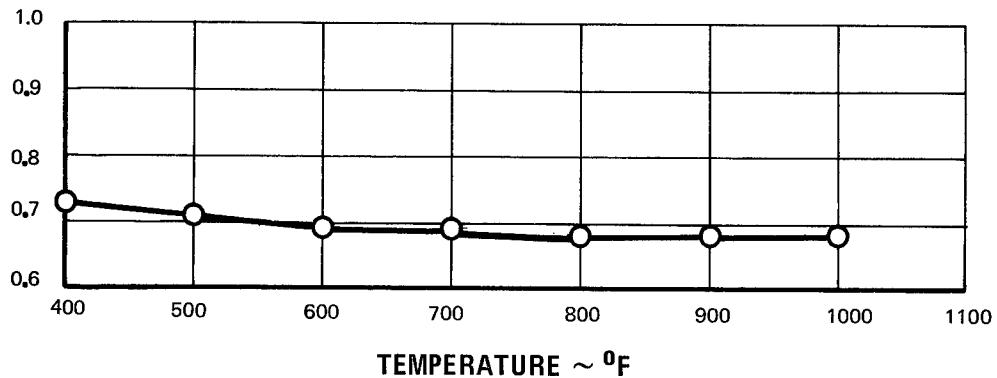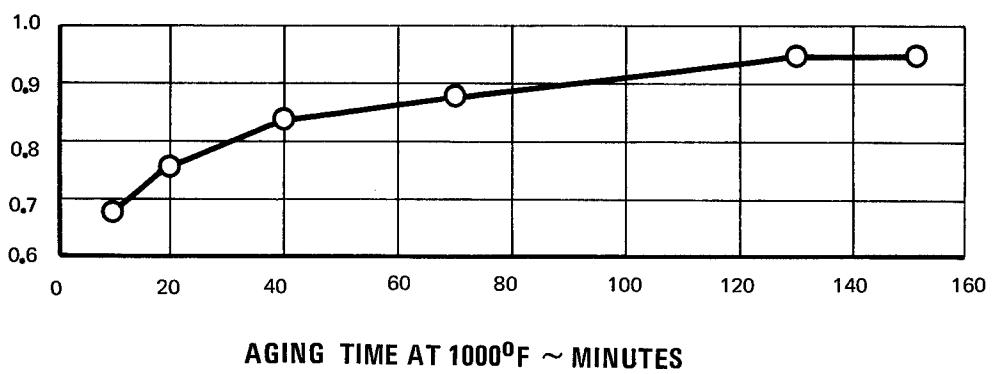
TOTAL HEMISPHERICAL EMITTANCE ~ ϵ_{TH}
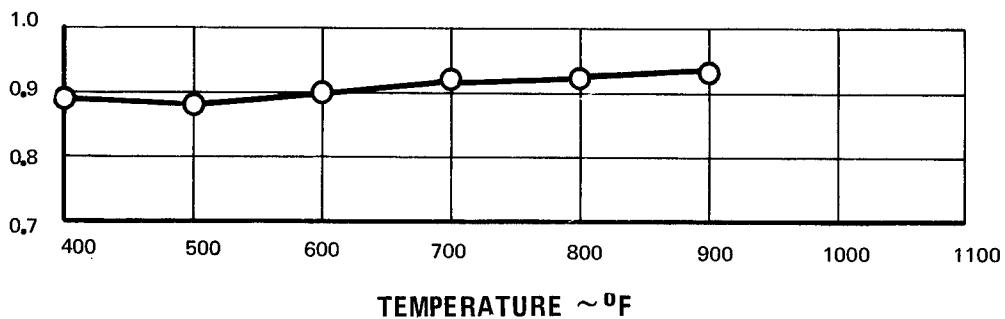
Figure 7   Total Hemispherical Emittance Measurement Results for Calcium-Titanate-Coated Beryllium Plates Using Thermal Decay Method

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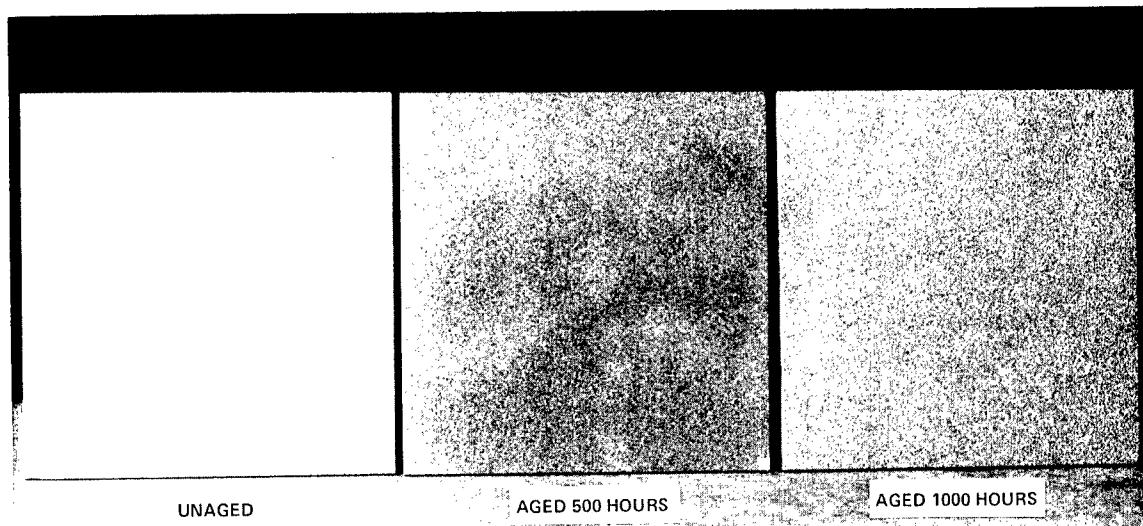
Mag: 0.5X

Figure 8   Appearance of Iron-Titanate-Coated Beryllium Plates Before Aging
and After Aging at 1200°F for 500 and 1000 Hours

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TABLE V

PARTICLE SIZE DISTRIBUTION OF IRON-TITANATE POWDER
USED FOR BERYLLIUM STUDIES

Particle Size (Microns)	Cumulative Weight Percent
72	37
66	44
60	54
52	63
42	74
33	82
26	88
21	90
17	94
9.5	99
4.1	100

b. Aging Tests

Iron-titanate-coated beryllium plates (three inches square by 0.10 inch thick) were aged at 800°F for periods of 100, 500, and 1000 hours and at 1200°F for 500 and 1000 hours. An attempt was made to age three specimens at 1400°F before the decision was made to limit the maximum aging temperature to 1200°F. However, faulty instrumentation resulted in overheating of the specimen, and aging actually occurred at 1500°F. At this temperature, extensive vaporization of the beryllium occurred. No analyses were performed on this specimen.

With the exception of the specimen aged above 1400°F, none of the specimens showed any cracking or spalling following aging. The only effect of aging was a slight darkening of the coatings. Typical specimens are shown in Figure 8.

The weights of the specimens before and after aging are shown in Table VI. All specimens lost between 0.002 and 0.007 gram, which represents an identifiable weight change, but an insignificant amount in relation to the total specimen weight.

TABLE VI

WEIGHTS OF IRON-TITANATE-COATED BERYLLIUM
SPECIMENS BEFORE AND AFTER AGING

Specimen	Test Temperature (°F)	Test Hours	Weight (gm) Before Test	Weight (gm) After Test	Percent Change in Weight	Average Percent Change in Weight	Gross Change in Weight (mg/yr)
1	800	100	30.356	30.350	0.02		
2	800	100	30.451	30.448	0.01	0.02	1752
3	800	100	29.929	29.924	0.02		
4	800	500	30.367	30.360	0.02		
5	800	500	30.165	30.161	0.01	0.02	350
6	800	500	30.117	30.111	0.02		
7	800	1000	30.570	30.567	0.01		
8	800	1000	30.456	30.454	0.01	0.01	88
9	800	1000	30.103	30.100	0.01		
10	1200	500	30.391	30.388	0.01		
11	1200	500	29.979	29.977	0.01	0.01	175
12	1200	500	29.188	29.181	0.02		
13	1200	1000	29.927	29.925	0.01		
14	1200	1000	30.093	30.090	0.01	0.01	88
15	1200	1000	29.594	29.590	0.01		

The results of the spectrographic analyses are presented in Table VII. Aging revealed the presence of small amounts of chromium and zirconium which were not detected in the coating before aging. These elements may have been present in the sprayed coating as nonhomogeneous impurities introduced during the spraying operation or during sample preparation prior to analysis. In any event, their concentrations are not sufficient to affect the coating properties detrimentally. X-ray diffraction analysis detected the presence of no phases other than Fe_2TiO_5 in any of the coatings.

TABLE VII

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF IRON TITANATE APPLIED
TO BERYLLIUM

	Impurity Content (Weight Percent)							
	Al	Cr	Cu	Mg	Mn	Ni	Si	Zr
As Sprayed	0.5	trace	0.01	0.2	0.5	trace	0.4	0
500 Hours at 800°F	0.8	0.3	0.01	0.2	0.5	0.1	0.3	0.1
1000 Hours at 800°F	0.7	0.15	0.01	0.15	0.4	0.1	0.2	0.1
500 Hours at 1200°F	1.0	0.5		0	0.2	0	0.5	0
1000 Hours at 1200°F	0.7	0.3	0	0.3	0.4	0	0.4	0

Examination of the microstructures of the specimens revealed no changes from those of unaged specimens. Typical photomicrographs of specimens aged for 1000 hours at 800°F and 1200°F are shown in Figure 9. The beryllium for the specimen tested at 1200°F was received in the second shipment.

One of the specimens aged for 1000 hours at 1200°F was analyzed by electron-beam microprobe analysis for the concentrations of iron and titanium. The results are presented in Table VIII. As shown, the iron gradient extended from a concentration of 0.02 percent at the surface to less than 0.01 percent at a depth of 0.2 mil. The titanium concentrations were slightly higher. At the surface, the concentration was 0.05 percent, but the concentration was below the 0.01 percent minimum detection level of the apparatus at a depth of 0.28 mil. Point concentrations of iron and titanium were detected at several random locations within the substrate. These are believed to be precipitates present as impurities in the substrate before coating. They are clearly outside of the diffusion pattern observed and are not believed to be associated with the coating. It must be emphasized that the concentrations of iron and titanium are extremely small and confined to a very small depth beneath the surface. They do not indicate a significant amount of diffusion, nor is it felt that sufficient concentrations are present to affect the substrate properties detrimentally.
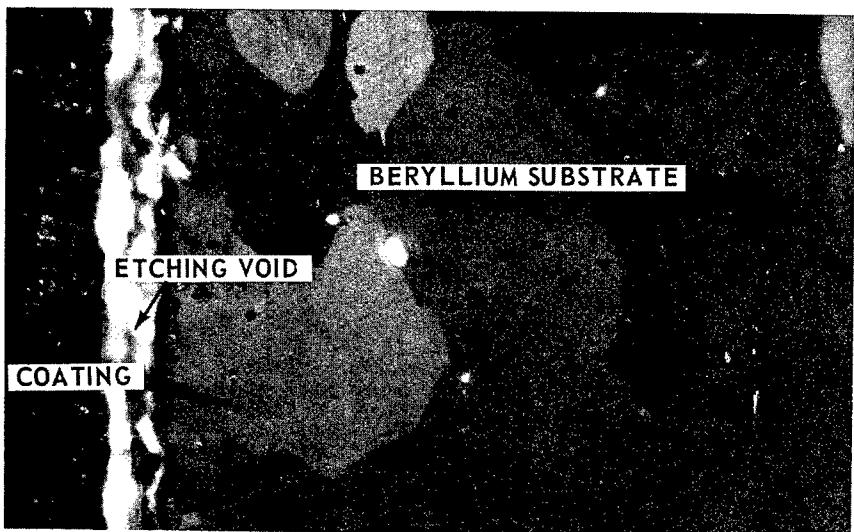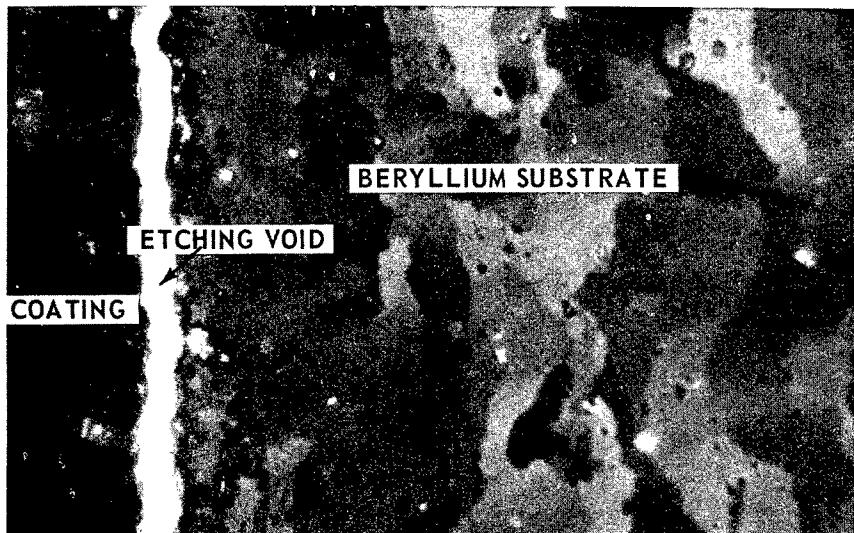
Etchant: 49% NH$_2$SO$_3$H, 16% H$_2$C$_2$O4, 1% HF, 34% H$_2$O   Mag: 200X

Figure 9   Typical Cross Sectional Photomicrographs of Iron–Titanate–Coated
Beryllium Plates Aged for 1000 Hours at 800°F (Top) and 1200°F
(Bottom)

TABLE VIII

CONCENTRATIONS OF IRON AND TITANIUM ACROSS BERYLLIUM PLATE COATED WITH IRON TITANATE AND AGED AT 1200°F FOR 1000 HOURS

Depth Below Interface (Mils)	Concentration (Weight Percent)	
	Iron	Titanium
0	0.02	0.05
0.07	0.01	0.03
0.14	0.01	0.01
0.21	0	0.01
0.28	0	0
0.35	0	0
0.42	0.03	0.01
0.49	0.04	0.01
0.57	0	0.01
0.64	0.04	0.01
0.71	0	0.01
0.78	0	0
0.92	0	0
1.1	0	0
1.2	0	0
1.3	0	0
1.5	0	0
1.6	0	0
1.8	0	0
2.1	0	0
2.4	0	0
2.8	0	0.2
3.1	0	0

Note: Minimum detectable concentrations of iron and titanium are 0.01 weight percent. Concentrations below this level are reported as 0.

c. Emittance Testing

The emittance of iron-titanate-coated beryllium was measured through steady-state testing and through thermal-decay testing. The emittance values obtained are shown in Figure 10.

BEFORE AGING

INCREMENTAL TEMPERATURE ENDURANCE TEST

AFTER AGING 1000 HOURS AT 1200°F
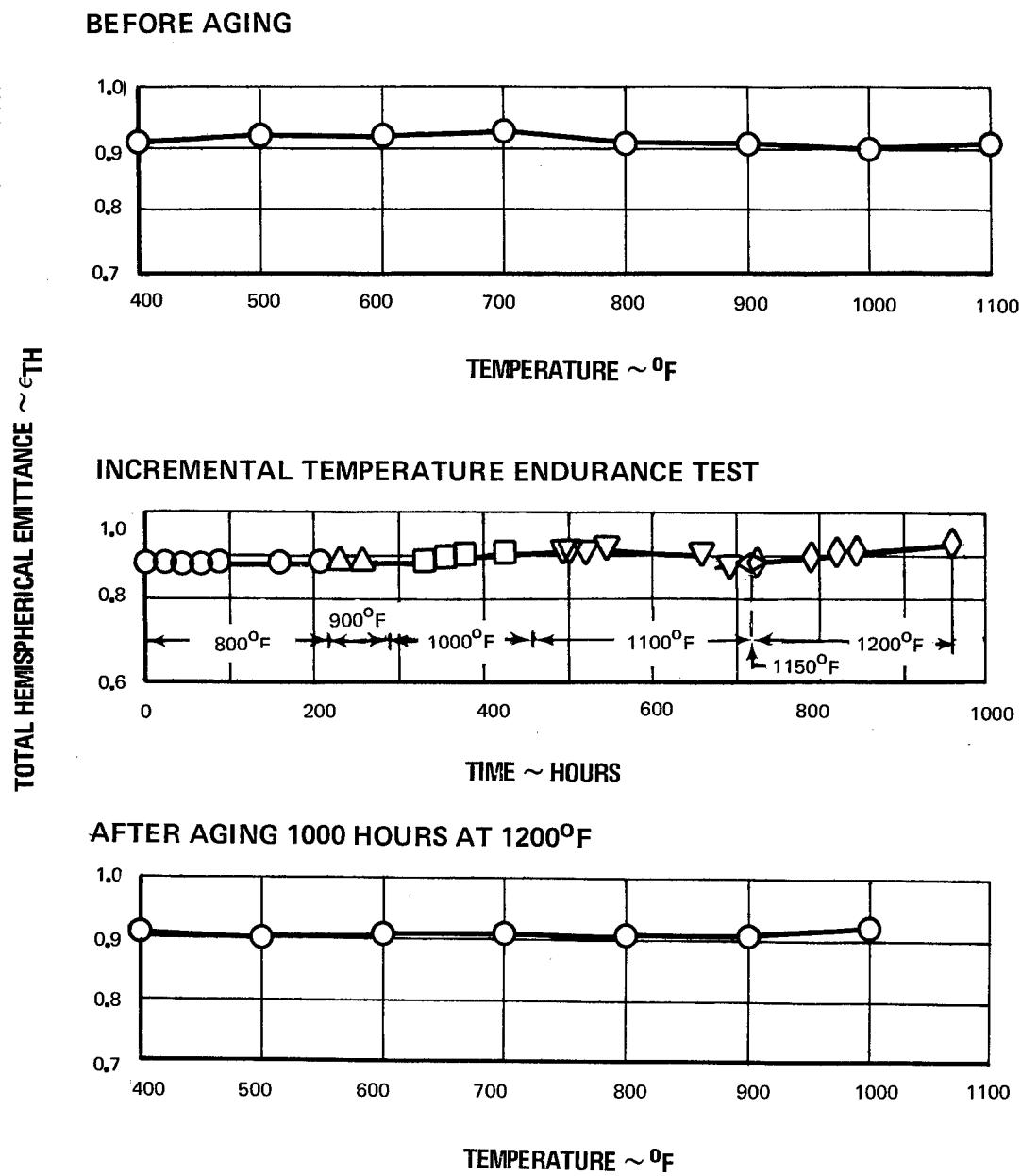
Figure 10   Total Hemispherical Emittance Measurement Results for Iron-Titanate-Coated Beryllium

As shown, two beryllium plates were tested by the thermal decay method. One plate was unaged, and the other was aged for 1000 hours at 1200°F before testing. In both cases, the emittance was about 0.91 over the entire temperature range from 400°F to 1000°F. In addition, a beryllium strip coated with iron titanate was tested for 970 hours. This specimen demonstrated an emittance between 0.88 and 0.91 for temperatures between 800°F and 1200°F.

3. Zirconium-Titanate Coating on Beryllium

a. Material Description

The zirconium titanate material was obtained from the Zirconium Corporation of American. X-ray diffraction analysis indicated that $ZrTiO_4$ was the only phase present, and spectrographic analysis detected the presence of 0.3 percent silicon, 0.01 percent magnesium, 0.3 percent aluminum, 0.6 percent hafnium, and traces of iron and manganese. The particle size distribution of the powder as determined by screen analysis is shown in Table IX.

TABLE IX

PARTICLE SIZE DISTRIBUTION OF
ZIRCONIUM TITANATE POWDER

Particle Size (Microns)	Cumulative Weight Percent
63	32.0
50	84.0
40	93.0
32	95.0
25	96.0
20	99.0
17	100.0

Note: Powder obtained from Zirconium Corporation of America

b. Aging Tests

The zirconium-titanate-coated beryllium plates were aged at 800°F and 1200°F for 100, 500, and 1000 hours. After aging, the specimens aged for the longer periods and at the higher temperature were slightly darker than the unaged specimens, but the color change was small, as shown in Figure 11. In no case was there any cracking, spalling, or other indication of coating separation.

UNAGED   AGED 100 HOURS   AGED 500 HOURS   AGED 1000 HOURS
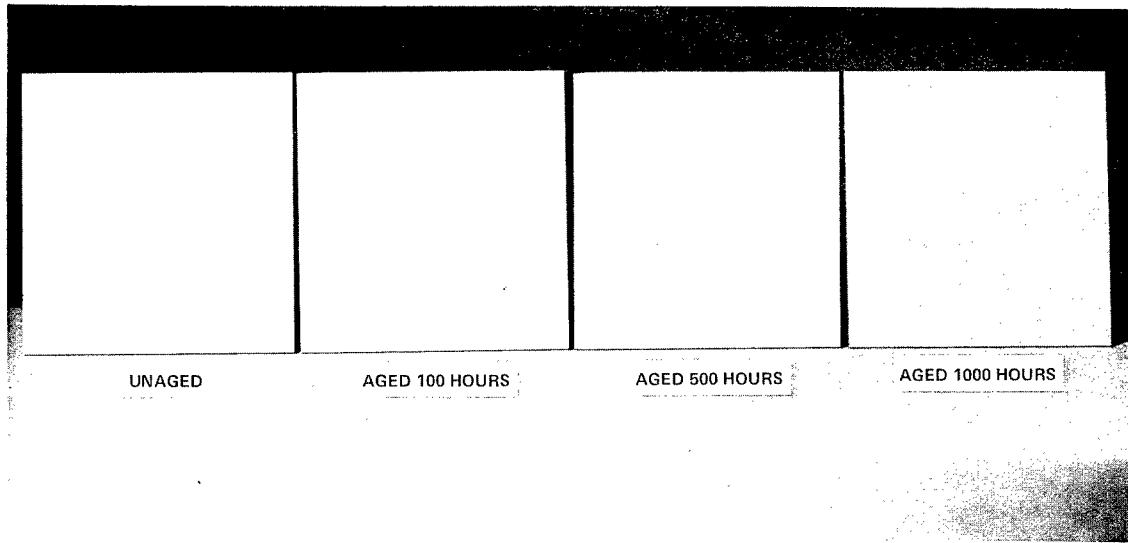
Mag: 0.4X

Figure 11   Appearance of Zirconium-Titanate-Coated Beryllium Plates Before
Aging and After Aging at 1200°F for 100, 500, and 1000 Hours

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The weights of the specimens before and after aging are shown in Table X.
Similar to the other specimens, the zirconium-titanate-coated plates generally
lost small amounts of weight during aging. Weight losses ranged from 0 to 0.006
gram, which represents an insignificant weight change in relation to the total
weight of the specimen.

Spectrographic analysis detected the impurities listed in Table XI. As shown, the
impurities in the aged coatings are about the same as those in the unaged coating.
X-ray diffraction analysis detected $ZrTiO_4$ as the only phase present in the coat-
ings. Photomicrographs were taken of all specimens, and the results revealed
no changes in microstructure caused by aging. Typical photomicrographs for
specimens aged at 800°F and 1200°F for 1000 hours are shown in Figure 12. The
beryllium for these specimens was received in the second shipment.

TABLE X

WEIGHTS OF ZIRCONIUM-TITANATE-COATED BERYLLIUM
SPECIMENS BEFORE AND AFTER AGING

Specimen	Test Temper- ature (°F)	Test Hours	Weight (gm) Before Test	Weight (gm) After Test	Percent Change in Weight	Average Percent Change in Weight	Gross Change in Weight (mg/yr)
1	800	100	29.283	29.284	0		
2	800	100	29.590	29.589	0	0	0
3	800	100	30.018	30.018	0		
4	800	500	29.783	29.777	0.02		
5	800	500	30.041	30.035	0.02	0.02	350
6	800	500	30.145	30.139	0.02		
7	800	1000	30.863	30.860	0.01		
8	800	1000	29.740	29.737	0.01	0.01	88
9	800	1000	29.275	29.272	0.01		
10	1200	100	29.960	29.958	0.01		
11	1200	100	29.740	29.737	0.01	0.01	876
12	1200	100	29.736	29.735	0		
13	1200	500	29.746	29.742	0.01		
14	1200	500	29.839	29.835	0.01	0.01	175
15	1200	500	29.835	29.832	0.01		
16	1200	1000	29.551	29.551	0		
17	1200	1000	30.195	30.194	0	0	0
18	1200	1000	29.635	29.634	0		

TABLE XI

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF ZIRCONIUM TITANATE APPLIED
TO BERYLLIUM

	Impurity Content (Weight Percent)						
	Al	Cu	Fe	Hf	Mg	Mn	Si
Unsprayed Powder	0.3	0	trace	0.6	0.01	trace	0.3
As Sprayed	0.1	0	0.1	0	0.1	trace	0.05
100 Hours at 800°F	0.1	0	0.1	0	0.1	trace	0.05
500 Hours at 800°F	0.2	0.01	0.1	0	0.01	trace	0.15
1000 Hours at 800°F	0.1	trace	0.05	0	trace	trace	trace
100 Hours at 1200°F	0.05	0.01	0.02	0	trace	trace	trace
500 Hours at 1200°F	0.2	0.01	0.02	0	0.01	trace	0.15
1000 Hours at 1200°F	0.05	trace	trace	0	trace	trace	trace
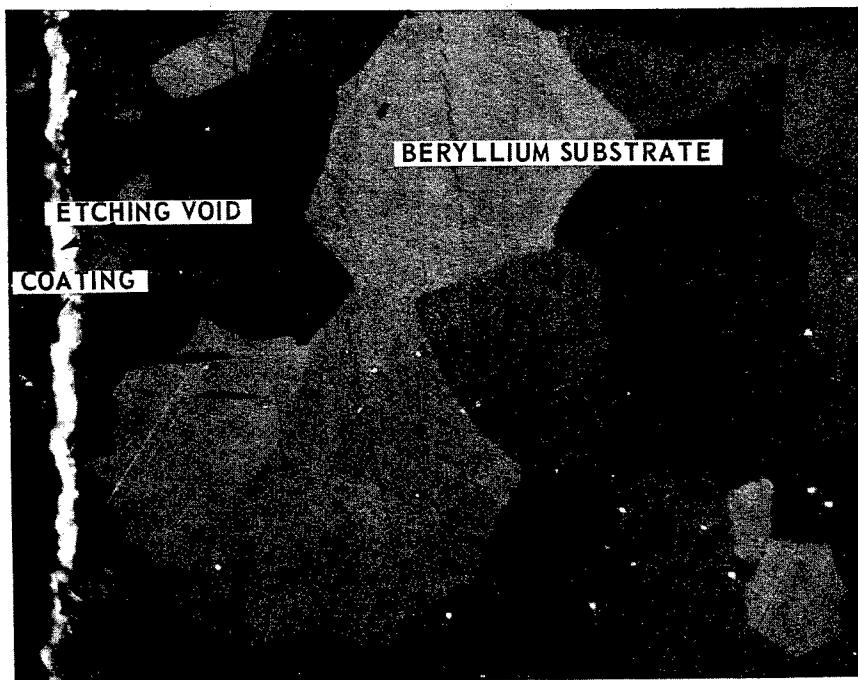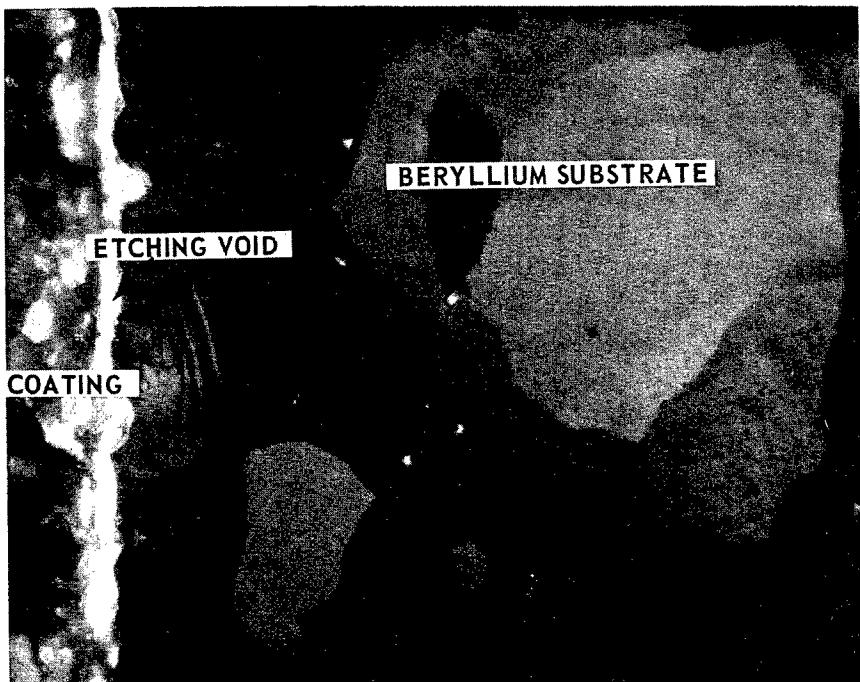
Mag: 200X

Echant: 49% NH_2SO_3H, 16% $H_2C_2O_4$, 1% HF, 34% H_2O

Figure 12   Typical Cross Sectional Photomicrographs of Zirconium-Titanate-
Coated Beryllium Plates Aged for 1000 Hours at 800°F (Top) and
1200°F (Bottom)

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An electron beam microprobe analysis was performed on a zirconium-titanate-coated beryllium plate which was aged for 1000 hours at 1200°F. The analysis determined the concentrations of zirconium and titanium in the beryllium. The results are presented in Table XII. As shown, a zirconium concentration of 1.01 percent was measured at the surface, but the concentration decreased to less than 0.02 percent at depths greater than 0.5 mil. The titanium concentration at the surface was found to be 1.69 percent, but the concentrations of zirconium and titanium within 0.2 mil of the surface are substantially higher than the concentrations of the coating constituents on other specimens. However, the higher concentrations extend only to a depth which is about equal to the roughness height of the substrate. The first coating applied to this specimen did not bond properly and was removed by grit blasting. On the basis of the microprobe analyses, it appears that minute particles of the first coating were imbedded into the substrate during grit blasting. Subsequent diffusion would produce the observed concentrations. In any event, the concentrations are extremely small and extend to very small depths, and, therefore, do not represent any substantial coating diffusion into the substrate.

TABLE XII

CONCENTRATIONS OF ZIRCONIUM AND TITANIUM ACROSS BERYLLIUM
PLATE COATED WITH ZIRCONIUM TITANATE AND AGED AT
1200°F FOR 1000 HOURS

Depth Below Interface (Mils)	Concentration (Weight Percent)	
	Zirconium	Titanium
0	1.01	1.69
0.7	0.59	0.83
0.14	0.29	0.39
0.21	0.10	0.16
0.28	0.60	0.06
0.35	0.03	0
0.40	0	0
0.50	0.04	0
0.80	0	0
1.20	0	0
1.60	0	0
1.90	0	0
2.30	0	0
2.40	0	0
2.60	0	0
6.1	0	0
13.2	0	0
20.3	0	0
38.0	0	0
56.0	0	0.07

Note: Minimum detectable concentrations of zirconium and titanium are 0.02 and 0.05 weight percent, respectively. Concentrations below these levels are reported as 0.

c. Emittance Tests

Total hemispherical emittance measurements were made on zirconium-titanate-coated beryllium specimens by the thermal decay method. Both unaged specimens and specimens which had been aged at 1200°F for 1000 hours were tested. The emittance values obtained were similar for both specimens, varying from 0.84 to 0.91 over the temperature range of 400°F to 900°F. These values are shown in Figure 13.
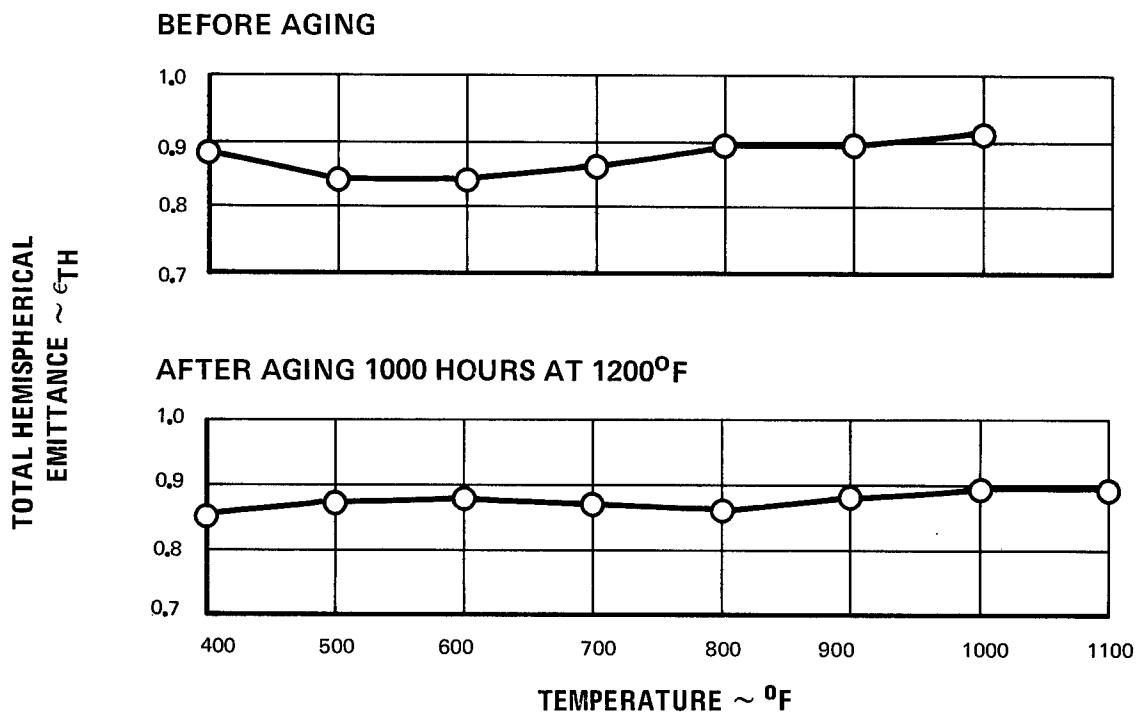
Figure 13   Total Hemispherical Emittance Measurement Results for Zirconium-Titanate-Coated Beryllium Plates

4. Anodized Beryllium

Anodized beryllium coatings were prepared in a 10 weight percent chromic acid solution at 65°F by the Summit Finishing Company in Thomaston, Connecticut.

Since anodized beryllium coatings had not been tested previously, a specimen was installed in the thermal decay emittance rig for emittance measurement. Subsequently, the specimen was aged at 900°F for about 3 hours, and then the emittance was measured again. The specimen outgassed during aging, and the coating color changed from black to brown. In addition, the emittance decreased from about 0.88 to 0.80. On the basis of the instability of the coating and the emittance, this coating was rejected as unsuitable for further study.

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5. Aluminum-Oxide-Aluminum-Titanate Coating on Beryllium

The aluminum oxide aluminum titanate was prepared by the Zirconium Corporation of America from 88 weight percent aluminum oxide and 12 weight percent titanium oxide. Emission spectrographic analyses detected 0.5 percent iron, 0.1 percent silicon, 0.6 percent magnesium, and a trace of manganese. The particle size distribution for the powder used for plasma spraying is shown in Table XIII.

TABLE XIII

PARTICLE SIZE DISTRIBUTION OF ALUMINUM OXIDE-ALUMINUM TITANATE POWDER

Particle Size (Microns)	Cumulative Weight Percent
63	0
50	17.0
40	71.0
32	100.0

Since the aluminum oxide aluminum titanate also had not been tested previously on any substrate, a coating of the material was applied to a columbium-1 percent zirconium tube for preliminary testing prior to coating on beryllium. The resulting specimen was subjected to a short-term emittance test. The emittance obtained was only about 0.75 between 800°F and 1200°F, and, therefore, this material was also rejected as unsuitable for use as a high emittance coating on beryllium.

F. CONCLUSIONS

The aging tests performed on coated beryllium plates demonstrated that beryllium is not suitable for space radiator use at a temperature of 1400°F because of excessive beryllium vaporization. Coatings of calcium titanate, iron titanate, and zirconium titanate were shown to be compatible with beryllium for at least 1000 hours at temperatures up to 1200°F, although the zirconium titanate appeared to form a weaker bond with the beryllium than did the other coating materials. Analysis of the beryllium after aging revealed no changes other than insignificant, but detectable, diffusion of the coating constituents across the coating-substrate boundary, and an almost negligible decrease in weight. The coatings were generally unchanged by aging except for a slight darkening in color. No spalling was observed. An exception was the calcium titanate coating for which aging permanentaly increased the emittance from 0.68 to 0.92. The emittance of both the iron-titanate coating and the zirconium-titanate coating was about 0.91 at 900°F. Coatings of anodized beryllium and aluminum oxide aluminum titanate were found to be unsuitable for use as high-emittance coatings on beryllium.

III. LONG-TERM EMITTANCE TESTS

A. INTRODUCTION

The long-term emittance tests involved the testing of four coated specimens at elevated temperature in vacuum for extended periods. Following testing, the specimens were subjected to a detailed metallurgical and chemical analysis.

The materials tested were selected initially on the basis of the results of previous emittance programs and on a search of the literature. Candidate materials selected on this basis were subjected to 250-hour short-term emittance tests to obtain an indication of their stability at elevated temperatures and to fatigue testing to determine the adherence of the coating to the substrate and to detect any adverse effects of the coating on the fatigue properties of the substrate. The four coating materials which appeared most promising on the basis of these tests were selected for long-term testing. These were iron titanate, calcium, titanate, zirconium diboride molybdenum disilicide, and aluminum oxide aluminum titanate.

All coating materials tested in this program were applied to tubes of AISI-310 stainless steel or columbium-1 percent zirconium. The specimens with AISI-310 stainless-steel substrates were tested at 1350°F, and the specimens with columbium-1 percent zirconium substrates were tested at 1700°F. All testing was performed in vacuums of 1×10^{-7} torr or better. The tests were originally scheduled to run for 5000 hours, but this was later extended to 10,000 hours for the specimens with columbium-1 percent zirconium substrates and to 20,000 hours for the specimens with AISI-310 stainless-steel substrates.

B. SPECIMEN PREPARATION

The specimens consisted of coated tubes which were 9 inches long, 0.250 inch in diameter, and had a wall thickness of 0.010 inch. The tubes were made of either columbium-1 percent zirconium or AISI-310 stainless steel and were ordered to the specifications shown below.

Columbium-1 Percent Zirconium		AISI-310 Stainless Steel	
Columbium	98.5% minimum	Chrome	24.00 to 26.00%
Zirconium	0.8 to 1.2%	Nickel	19.00 to 22.00%
Carbon	100 ppm maximum	Manganese	2.00% maximum
Nitrogen	300 ppm maximum	Silicon	1.50% maximum
Oxygen	300 ppm maximum	Carbon	0.25% maximum
Hydrogen	20 ppm maximum		

The tubes had two black-body holes 0.0235 inch in diameter through one wall at the midpoint. The holes were separated longitudinally by 0.0522 inch and were displaced laterally by 0.043 inch from the tube centerline. The tubes were thoroughly cleaned in a saturated solution of concentrated sulfuric acid and potassium dichromate to remove organic contaminants before the coating was applied. They were then grit blasted with 60 mesh silicon carbide at 100 psi to a roughness height of 110 microinches as determined by a profilometer using arithmetic averaging.

All of the coatings for this program were applied by plasma-arc spraying. Plasma-arc spraying utilizes the high energy of an electric arc to ionize a gas and form a plasma. The energy of the plasma is released as heat. The coating material, in powder form, is propelled through the plasma, where it absorbs heat and melts, and subsequently strikes the specimen surface. The high temperatures attainable and the nonoxidizing atmosphere provided by plasma-arc spraying were more suitable for the intended application than the conditions produced by flame spraying. The coatings tested were applied by Pratt & Whitney Aircraft using Plasmadyne equipment. Details of the coating procedure are presented in Appendix A.

After being coated, the tubular specimens were flattened for 3/4 inch at each end to facilitate clamping to the power electrodes in the test chamber. The flattening process resulted in removal of most of the coating in the clamping region, and any remaining residue was removed by abrading the contact surface to ensure good electrical contact. A few flakes of the coating removed in this operation were saved and analyzed for comparison with the analysis of the coating after the test.

The black-body holes were reamed after the coating was applied to remove any coating material that might have accumulated during the coating process.

Subsequently, the locations for attaching thermocouples and voltage leads were marked on each specimen, and the coating was removed from a rectangular area measuring 0.010 x 0.030 inch at each location by means of a tungsten-carbide scraping tool. The thermocouple and voltage leads were attached by resistance welding. The distance between the voltage leads was then measured with a measuring microscope to allow precise calculation of the test section radiating area.

The specimens tested during the material selection process and subjected to 250-hour short-term endurance tests were instrumented with three platinum-platinum 10 percent rhodium thermocouples and two voltage leads. The specimens subjected to long-term endurance tests were instrumented with seven platinum-platinum 10 percent rhodium thermocouples and five Chromel-Alumel thermocouples. For these specimens, two thermocouple wires were used as voltage leads.

C. TEST APPARATUS AND PROCEDURES

1. Short-Term Endurance Emittance Test Chamber

The equipment used for conducting the 250-hour screening tests is shown in Figures 14 and 15. As shown, the emittance test chamber consisted of a vacuum chamber with support structures for the specimen and instrumentation, an evacuation system, a specimen heating power supply, and temperature measurement instrumentation.
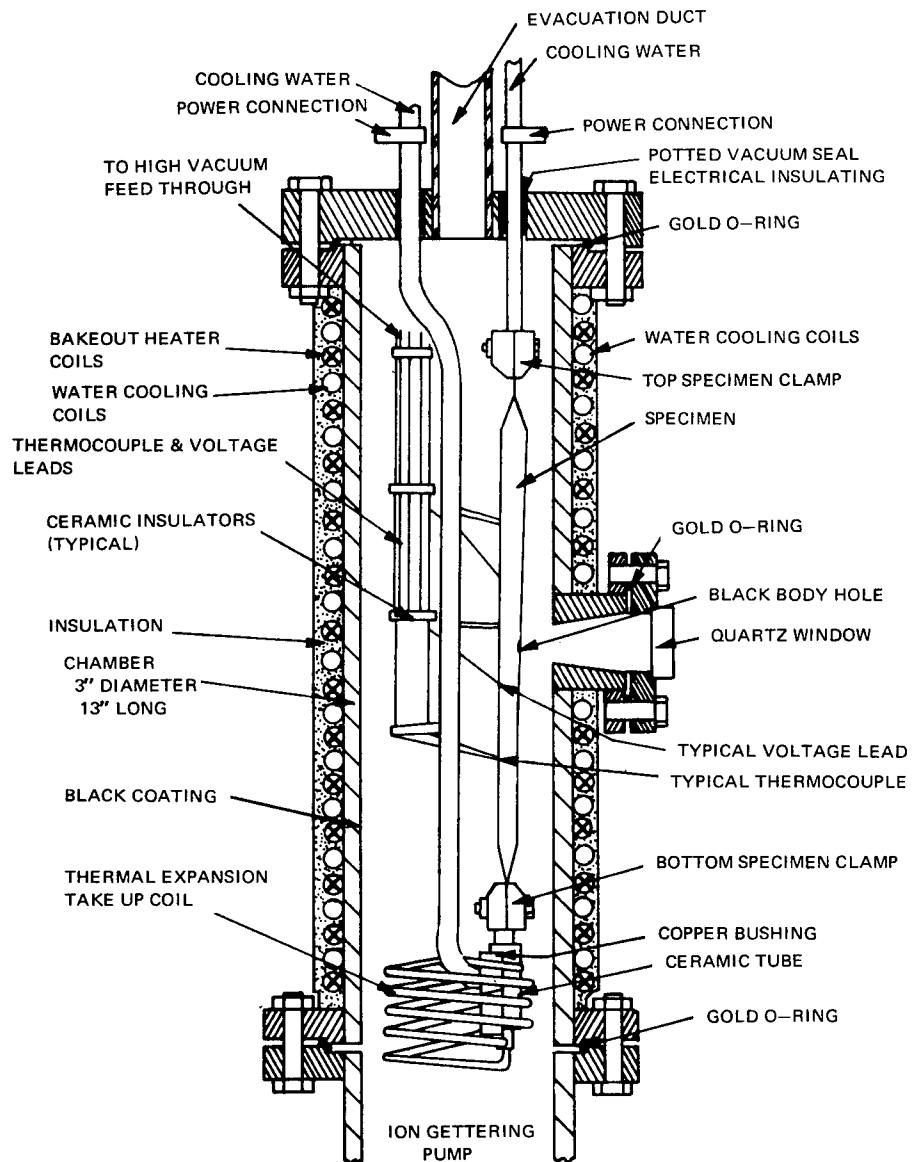
Figure 14 Sketch of Short-Term Endurance Emittance Test Chamber Showing the Relative Location of Specimen and Various Components
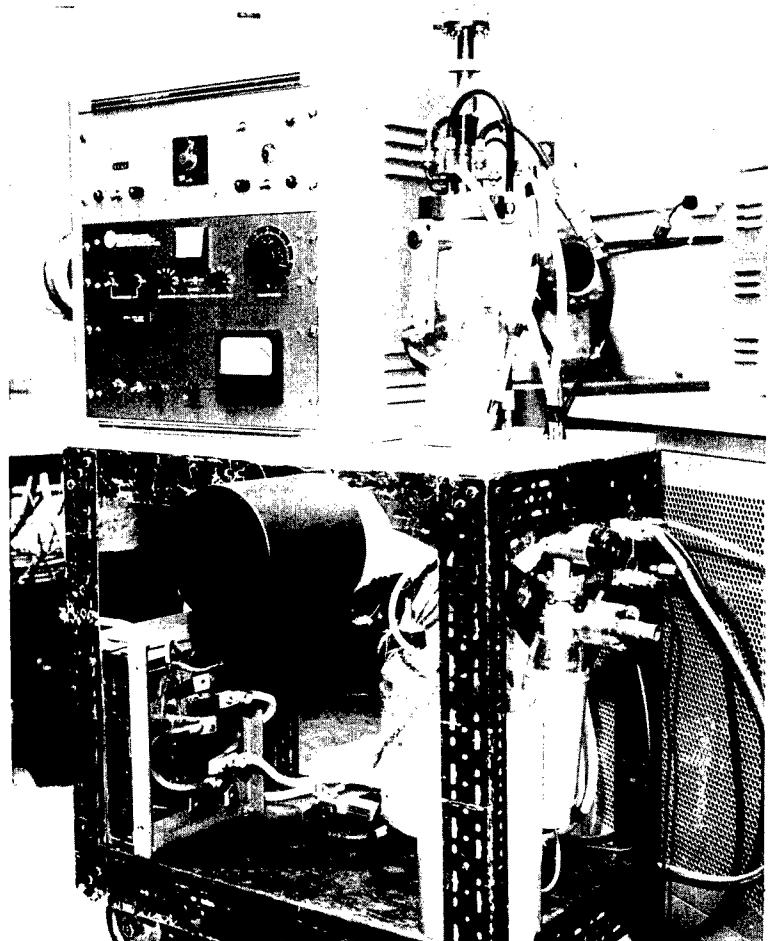
Figure 15 Short-Term Endurance Total Hemispherical Emittance Test Chamber   X-18512

The vacuum chamber was made of AISI-304 stainless steel and was 13 inches long with a 3-inch inside diameter. The inside wall was coated with "3M Black Velvet," which is a low reflectance coating with an emittance between 0.90 and 0.95 in the temperature range from 200 to 700°F. A viewing port for specimen observation and optical measurements was located at the midpoint of the chamber. The port consisted of an optically plane quartz window cemented to a stainless-steel cell with epoxy resin. The cell assembly was bolted and sealed with a gold O-ring to a mating flange, which was welded to a tubular extension from the chamber wall. The window was protected from condensate by a magnetically controlled rolling-disk shutter installed in a slot between the cell and the flange. The chamber was wrapped with 3/16-inch diameter copper tubing for water cooling to reduce the radiation from the walls, and a heating element was wound over the cooling coil to bake out the chamber during initial evacuation.

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The evacuation system consisted of a 40-liter-per-second ion-gettering pump and a titanium sublimation pump backed by a mechanical roughing pump and a liquid-nitrogen cold trap. The chamber pressure was measured by a Bayard-Albert type ionization gage and by measuring the ion-gettering pump current and determining the pressure from calibration curves.

The power supply for heating the specimens consisted of a multitap step-down power transformer, the primary of which was controlled by a variable auto-transformer. Power measurements were made by measuring the voltage drop across the specimen test section and across a current shunt by means of an AC-DC differential voltmeter. Thermocouple outputs for temperature measurement were measured with a slide-wire millivolt potentiometer used in conjunction with an ice-bath reference junction.

2. Fatigue Test Equipment

The bond strengths of the coatings were evaluated at room temperature in the fatigue test equipment shown in Figure 16. With this equipment, the specimens were vibrated at various stress levels at 120 cps. Both coated and uncoated specimens were tested, and the number of cycles to failure was plotted as a function of stress. Standard fatigue-test specimens (Figure 17) were machined and coated for these tests. Fracture represented failure for the uncoated specimens, whereas a coated specimen was considered to have failed as soon as cracking, spalling, or separation of the coating occurred, if these occurred before the substrate fractured.
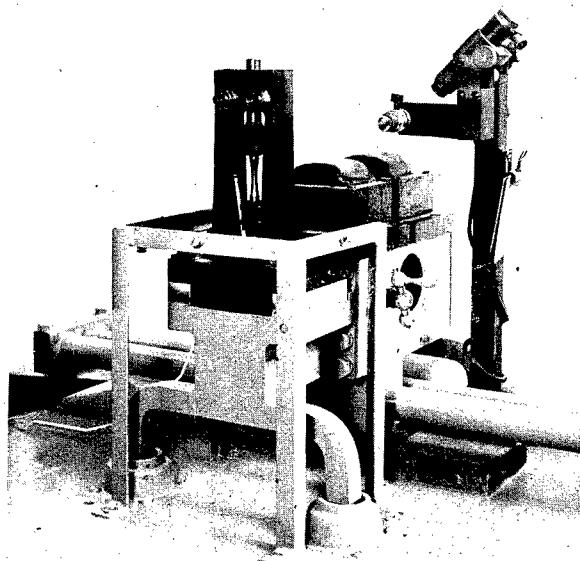
Figure 16 Westinghouse Vibration Fatigue Testing Machine   H-43337
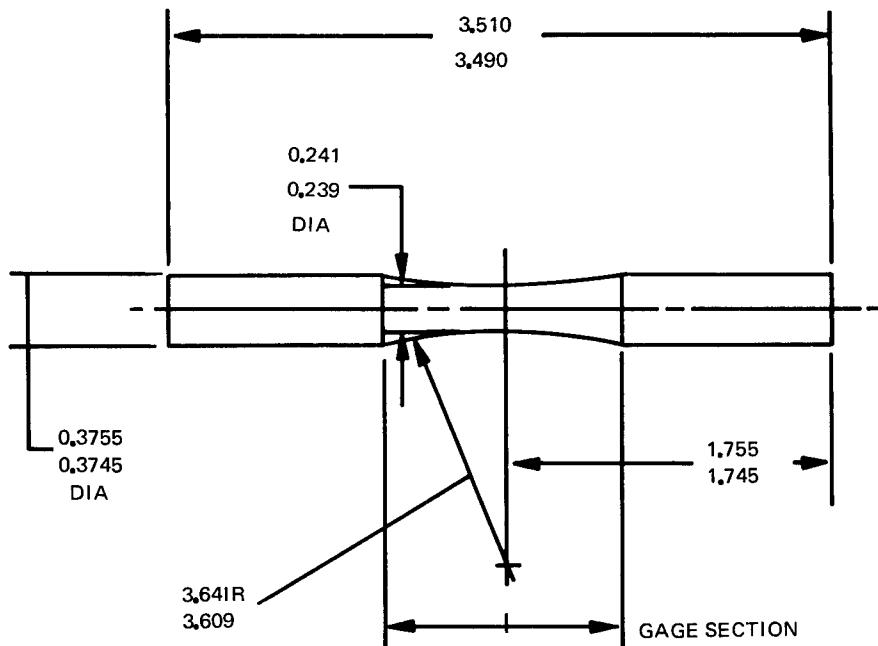
Figure 17 Westinghouse Round Bar Fatigue Specimen Design

The coated fatigue specimens were inspected at intervals for coating separation by heating them to red heat in vacuum and inspecting for lack of color uniformity. A lack of color uniformity qualitatively would indicate separation since any separation of the coating would lower the heat transfer rate between the substrate and the coating in the area where it occurred, resulting in a lower surface temperature and a dark spot in the area of separation. The specimens were photographed using infrared film to detect the nonuniformities not detectable visually and to provide a record of the test.

3. Long-Term Endurance Test Apparatus

The test equipment used for the long-term emittance tests is shown in Figure 18. The vacuum chambers for these units are 20 inches high and have inside diameters of 15 1/2 inches. These chambers are fabricated from AISI-304 stainless steel and coated with black paint. Each chamber has a 5.4-inch diameter window for observation of the specimen and for radiation measurements. The windows are protected by magnetically controlled shutters when not in use.

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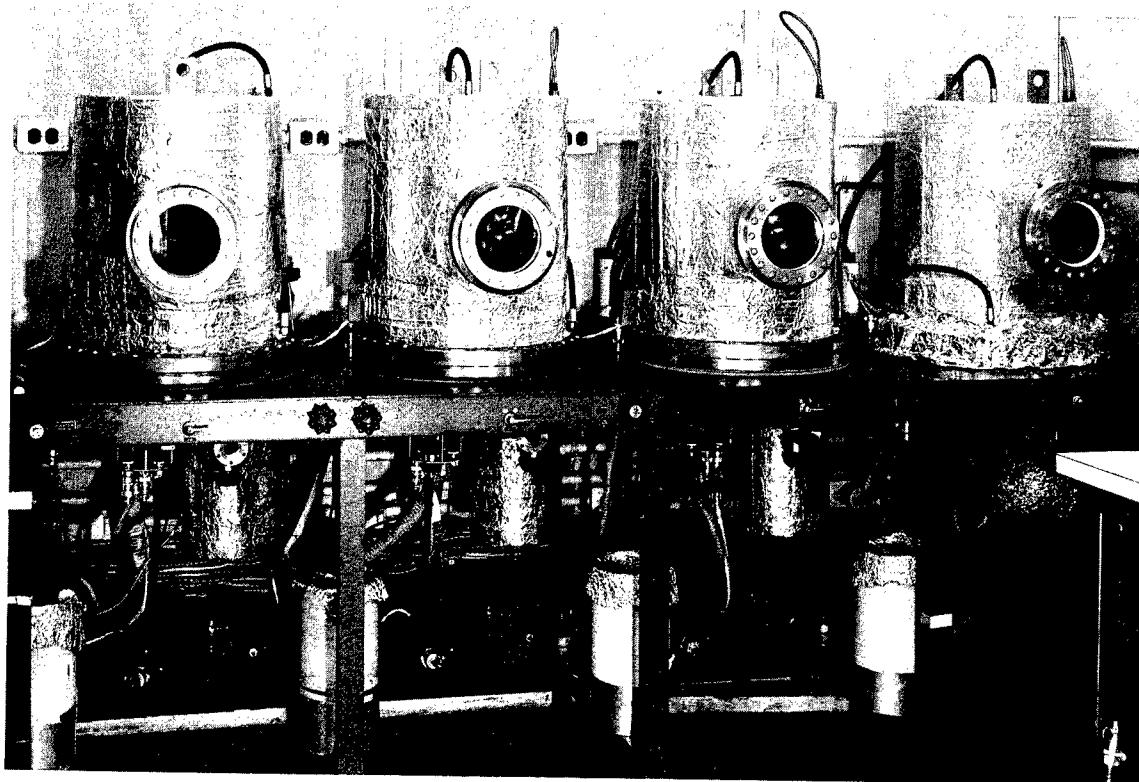
Figure 18 Long-Term Endurance Total Hemispherical Emittance Test Chambers
XP-23123

The evacuation system for each unit consisted of a 40-liter-per-second ion
gettering pump operated in conjunction with a mechanical vacuum pump with a
liquid-nitrogen cold trap. As for the short-term units, chamber pressures
were measured with a Bayard-Alpert type ionization gage and by measuring the
ion-gettering pump current.

All instrumentation readout equipment and chamber controls were located in the
control console shown in Figure 19. The instrumentation system included a
multipoint millivolt recorder, which, by means of a time-controlled stepping
relay, automatically recorded the chamber and specimen thermocouple outputs
hourly. A manually operated slide-wire potentiometer was used to provide high-
ly accurate temperature data for emittance calculations.
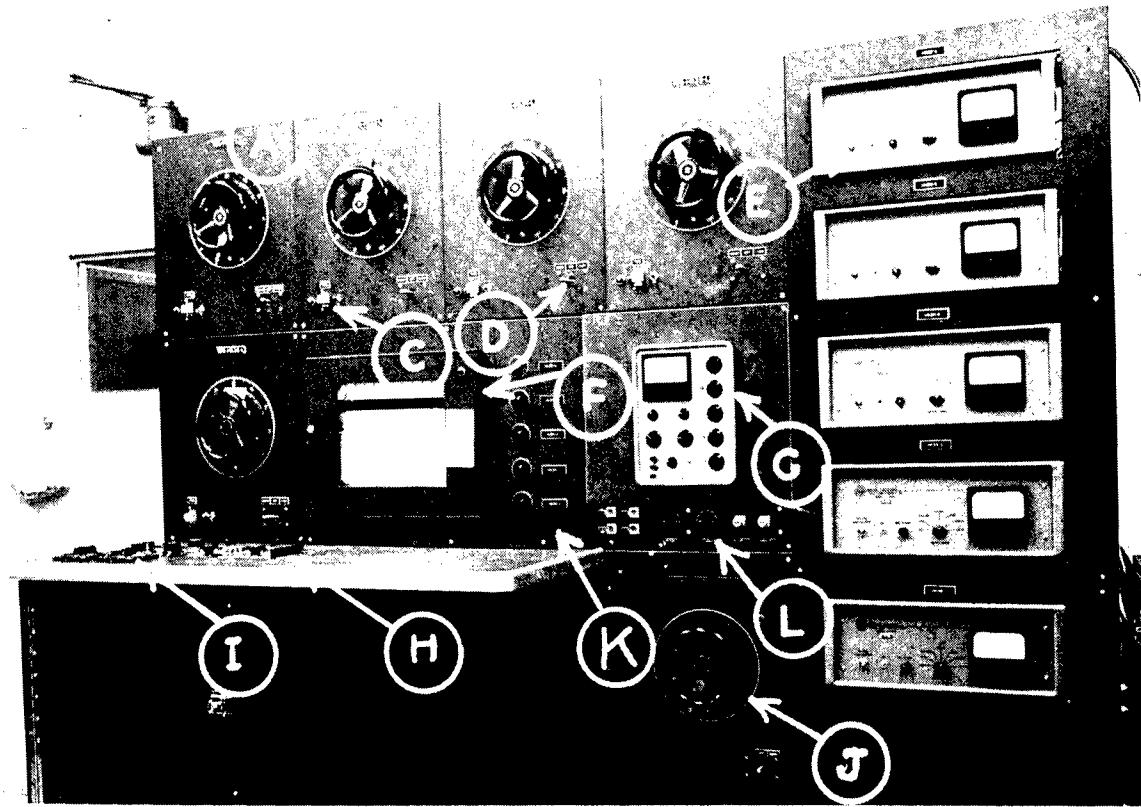
Figure 19   Control and Instrumentation Console for Endurance Test Chambers

A. Test Chamber Control Panel
B. Test Chamber Voltage Control
C. Cycle Timer
D. Voltage Switch
E. Vacuum Pump Power Supply
F. Multipoint Recorder

G. AC-DC Differential Voltmeter
H. Potentiometer
I. Thermocouple Selector Switch
J. Bake Out Heater Control
K. Thermocouple Mode Switch Panel
L. Specimen I and V Selection Panel

X-14520

D. COATING MATERIAL SELECTION AND PRELIMINARY SCREENING

Seven materials were selected for preliminary screening tests. These were iron titanate, calcium titanate, zirconium diboride-molybdenum disilicide, aluminum oxide-aluminum titanate, stabilized titanium oxide, zirconium titanate, and a barium titanate composition. All of these materials were applied to columbium-1 percent zirconium. In addition, iron titanate and calcium titanate were applied to AISI-310 stainless steel.

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1. Iron Titanate

The iron titanate used for these specimens was obtained from the Continental Coatings Corporation and was designated FCT-11. Analysis of the powder before use showed no crystalline phase other than iron titanate (Fe_2TiO_5) to be present. Emission spectrographic analyses detected the presence of 0.5 percent manganese, 0.1 percent magnesium, 0.7 percent aluminum, and 0.03 percent copper. The particle size distribution of the powder as determined by screen analysis is shown in Table XIV.

TABLE XIV

PARTICLE SIZE DISTRIBUTION OF
IRON TITANATE POWDER

Particle Size (Microns)	Cumulative Weight Percent
66	0
52	15.0
41	24.0
33	38.0
26	39.0
21	50.0
17	57.0
15	65.0
13	71.0
10	81.0
8	91.0
6	100.0

Two columbium-1 percent zirconium and one AISI-310 stainless steel tubes were coated with the iron-titanate material. Analysis of the coating from one end of one of the columbium-1 percent zirconium tubes indicated that iron titanate was the only phase present and that the same elements were present in about the same percentages as before spraying.

The initial test of the coated columbium-1 percent zirconium tube was terminated after 29.8 hours at 1800°F in a vacuum of 1 x 10^{-8} torr because a voltage lead failed. However, the emittance during the test was 0.86. The second test was

conducted for 200 hours at 1700°F and for 118 hours at 1800°F. The emittance values obtained during this test ranged from 0.86 to 0.88. The emittance remained steady at 0.88 for the last 100 hours. Visual examination of the specimen after testing revealed no changes in the specimen as a result of testing. The coating texture was the same as it was before testing, and no indications of cracking or spalling were present. Visual examination of the cold test chamber surfaces indicated that no coating vaporization had occurred.

The coated AISI-310 stainless steel tube was tested for 263 hours at 1350°F in a vacuum of 1 x 10^{-8} torr. The emittance values were about 0.90, but they were somewhat erratic. This erratic behavior was later found to be a result of faulty instrumentation. In order to be certain of the emittance, an additional 44-hour test was conducted at 1350°F after reinstrumentation. A constant emittance of 0.89 was measured. This specimen was subjected to thermal cycling after initial heating, after 100 hours, and after 200 hours. Examination after testing revealed no change in the appearance of the coating, and no cracking or spalling of the coating from the substrate was apparent.

Fatigue tests were conducted on coated and uncoated AISI-310 stainless steel and columbium-1 percent zirconium tubes. The results for the uncoated stainless steel specimens are shown in Figure 20. The run-out stress for this material appears to be about 50,000 to 55,000 psi. The results for the coated stainless steel specimens were similar, as shown in Figure 21. All of the coated specimens failed through fracture of the substrate. No failures resulted from spalling or cracking. A typical failed stainless-steel specimen is shown in Figure 22.
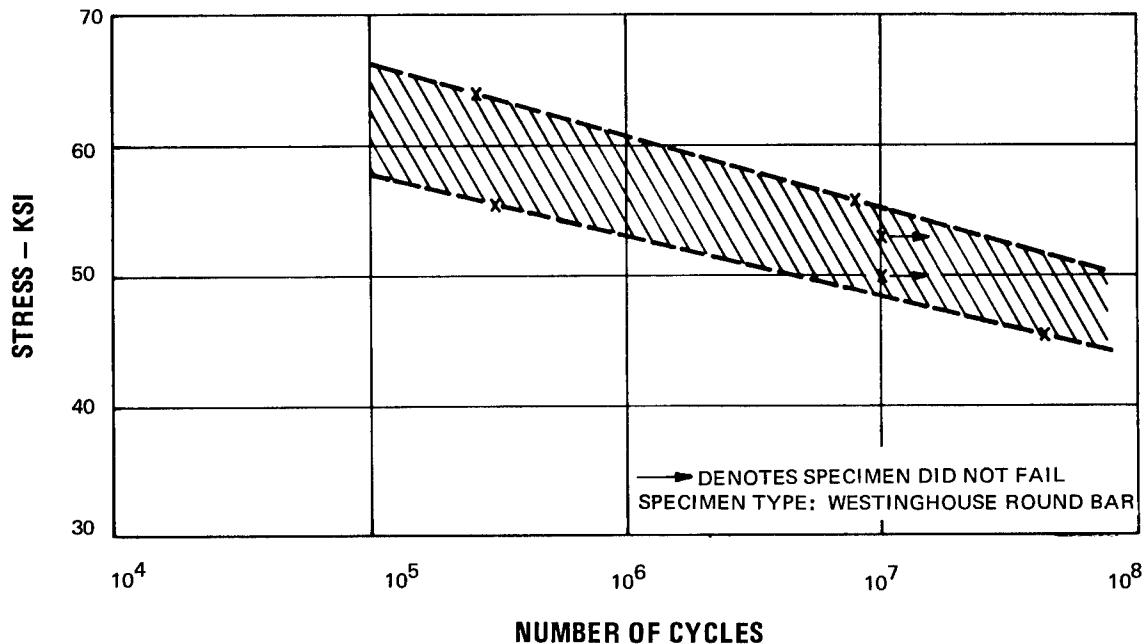
Figure 20   Fatigue Test Results Obtained at Room Temperature for AISI-310 Stainless Steel

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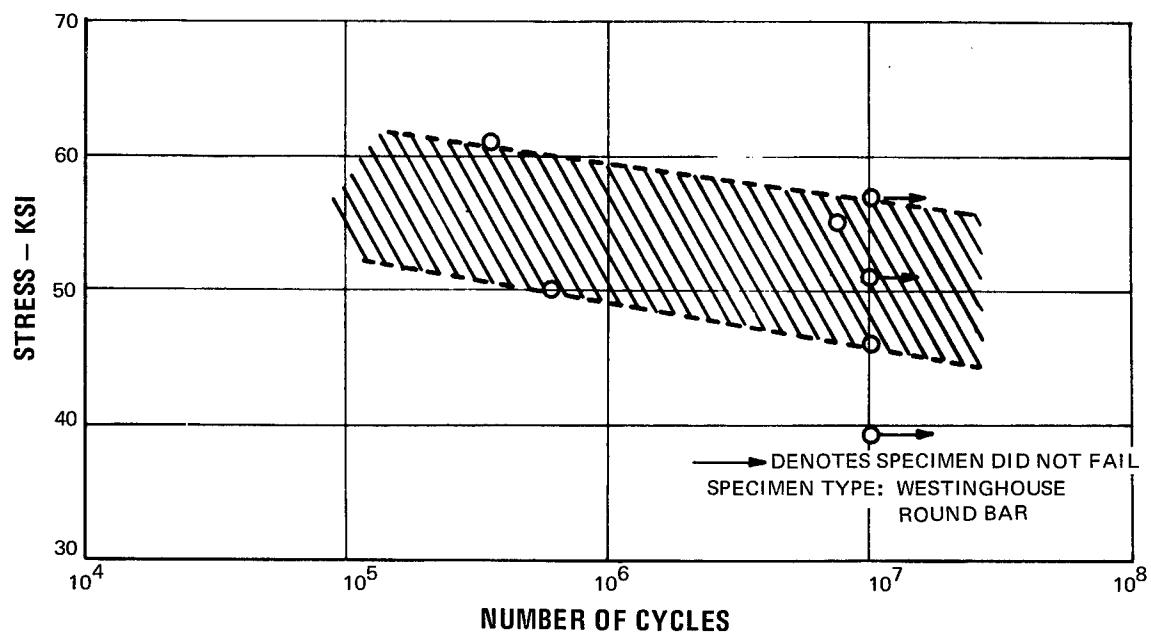
Figure 21   Fatigue Test Results Obtained at Room Temperature for AISI-310
Stainless Steel Coated with Iron Titanate
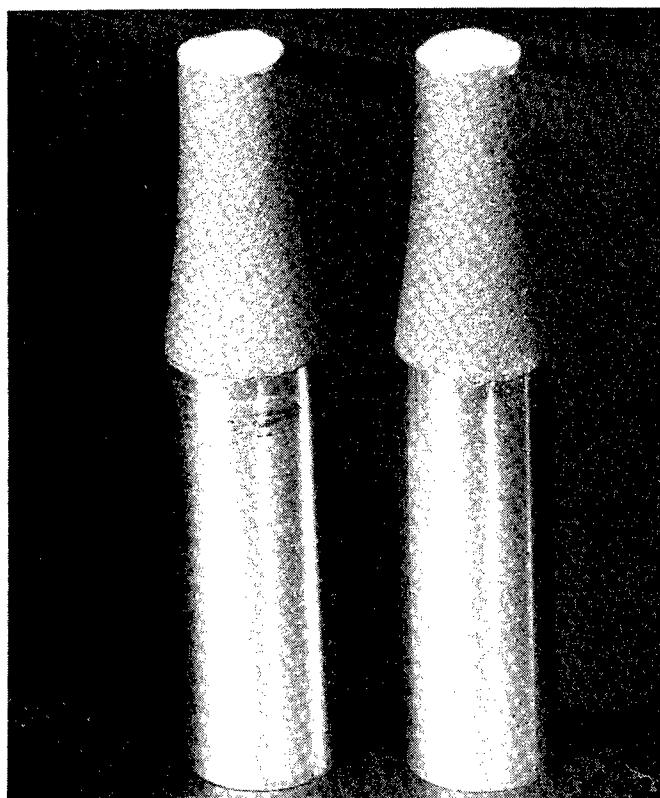
Figure 22   Fractured AISI-310 Stainless Steel Fatigue Specimen Coated with
Iron Titanate   XP-50601

Testing of the uncoated columbium-1 percent zirconium specimens indicated that the run-out fatigue stress for this material is 30,000 to 33,000 psi (see Figure 23). The coated specimens were found to have a run-out fatigue stress of 35,000 psi, which is about the same as that for the uncoated specimens (see Figure 24). In all cases, failure was the result of fracture of the substrate rather than spalling or cracking of the coating. A typical failed specimen is shown in Figure 25.
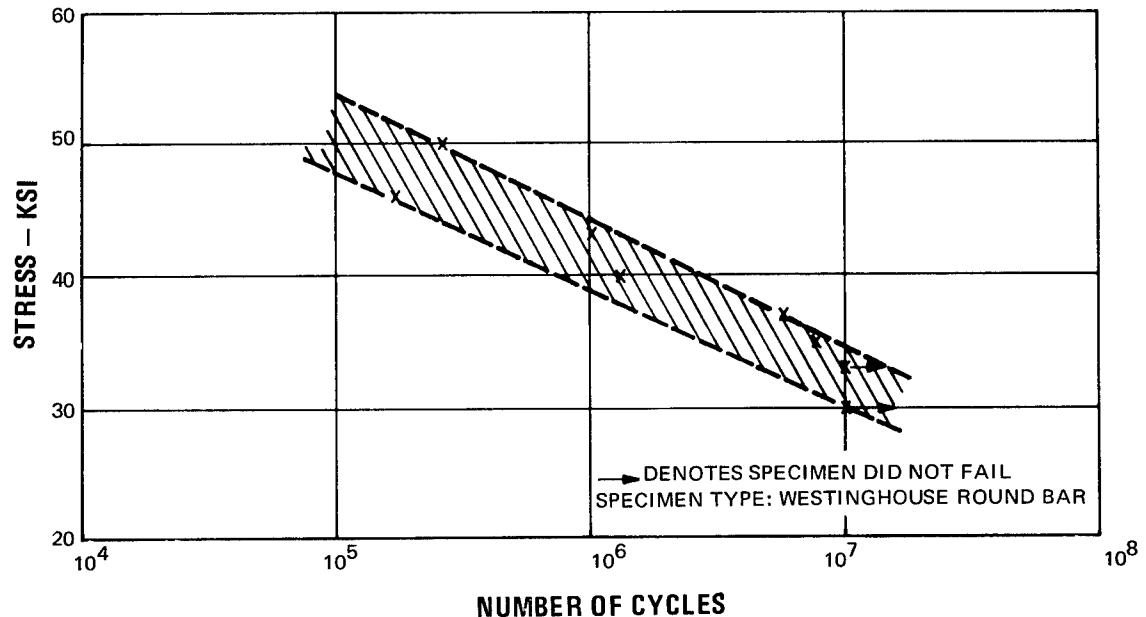
Figure 23   Fatigue Test Results Obtained at Room Temperature for Columbium-1 Percent Zirconium
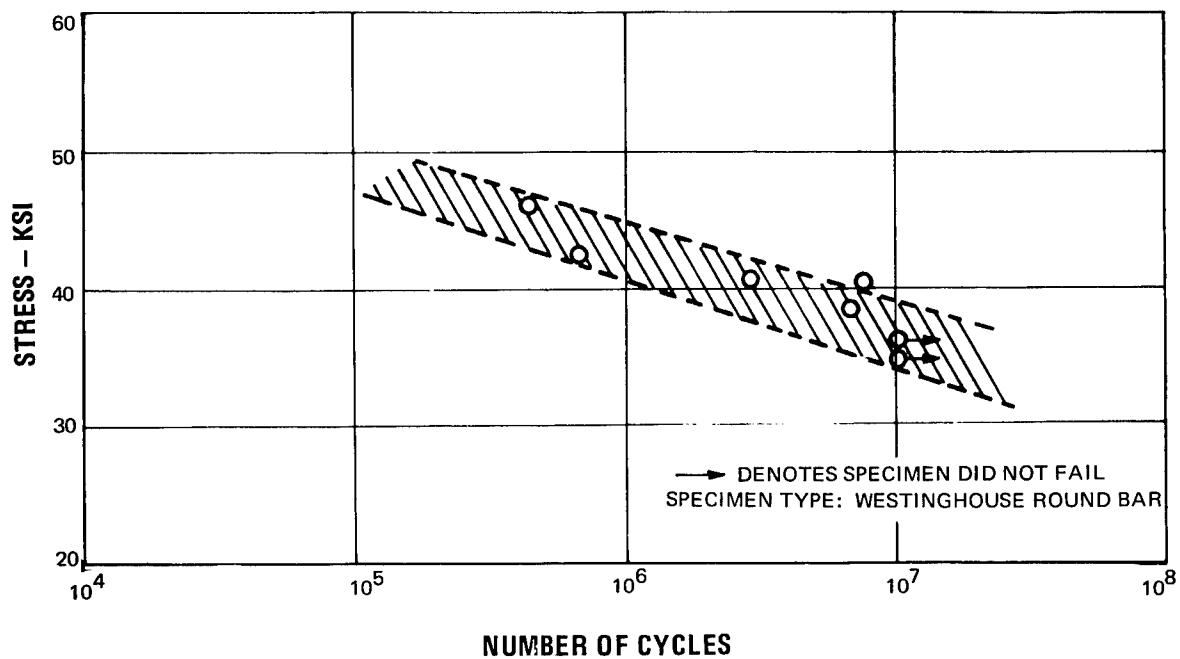
Figure 24   Fatigue Test Results Obtained at Room Temperature for Columbium-1 · Percent Zirconium Coated With Iron Titanate

44
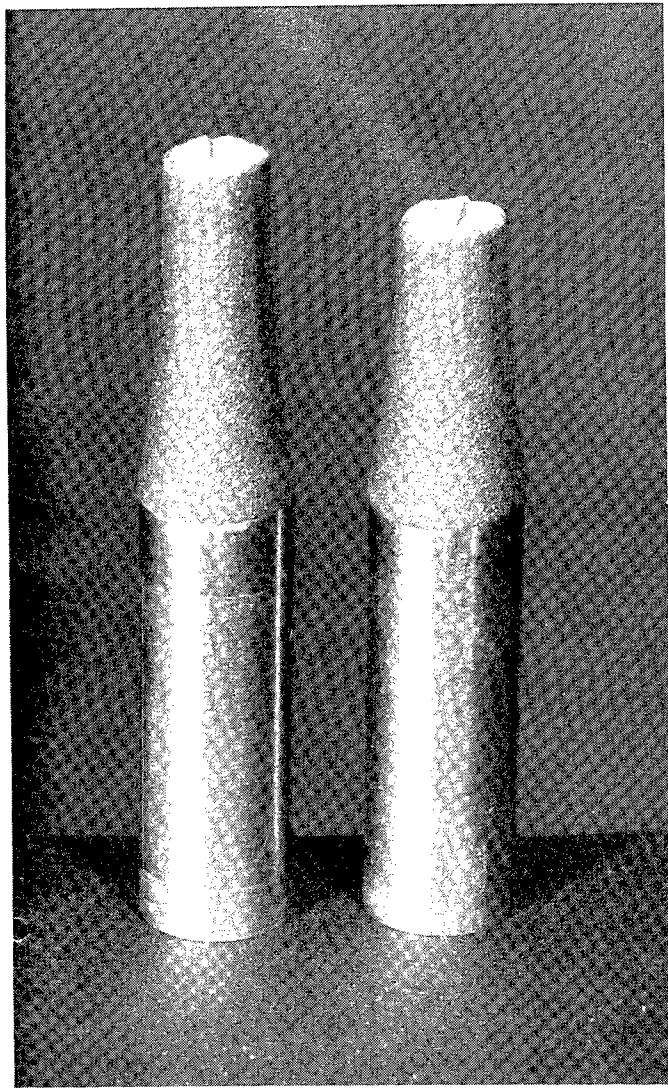
Figure 25   Fractured Columbium-1 Percent Zirconium Fatigue Specimen
              Coated with Iron Titanate   XP-50601

A coated AISI-310 stainless steel specimen which withstood 10^7 cycles at
52,000 psi without failure and a coated columbium-1 percent zirconium specimen
which withstood 10^7 cycles at 35,000 psi without failure were inspected while at
1500°F in vacuum.   The specimens are shown in Figures 26 and 27.   It is evident
from the uniform coloring that no separation occurred for either of these specimens.
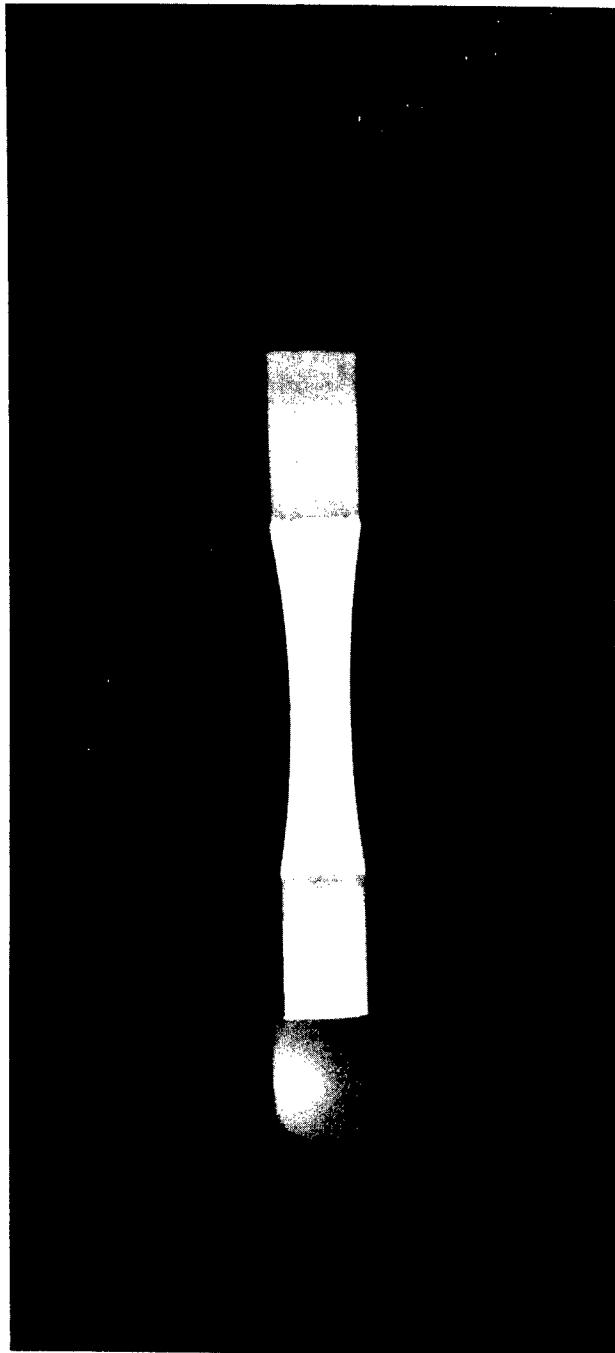
Figure 26   AISI-310 Stainless Steel Fatigue Specimen Coated With Iron Titanate
and Heated to 1500°F for Coating Separation Inspection
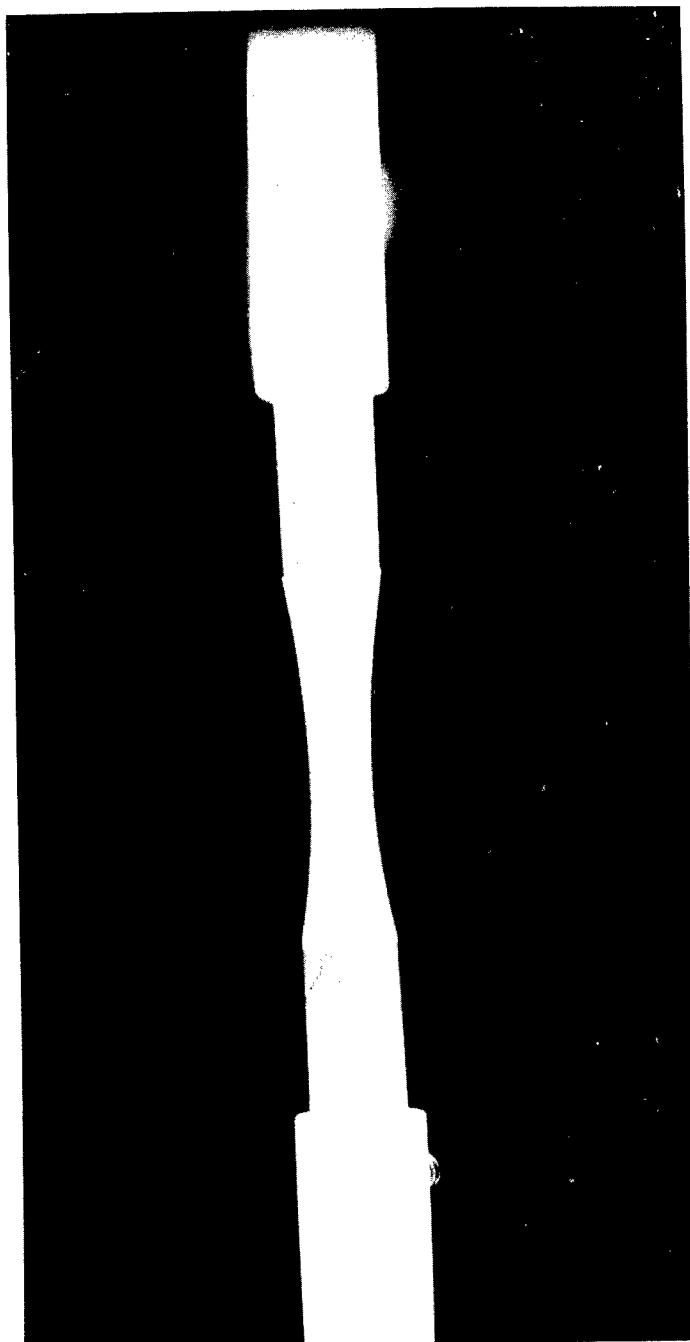
Figure 27   Columbium-1 Percent Zirconium Fatigue Specimen Coated With Iron
Titanate and Heated to 1500°F for Coating Separation Inspection

On the basis of the good emittance and adherence test results, both iron-titanate-coated AISI-310 stainless steel and iron-titanate-coated columbium-1 percent zirconium were selected for long-term emittance testing.

2. Calcium Titanate

The calcium titanate powder used was obtained from the Titanium Division of the National Lead Corporation. X-ray diffraction analysis detected $CaTiO_3$ as the only crystalline phase present, and emission spectrographic analysis detected only trace amounts of silicon and magnesium. The particle size distribution of the powder as determined by screen analysis is shown in Table XV.

TABLE XV

PARTICLE SIZE DISTRIBUTION OF
CALCIUM TITANATE POWDER

Particle Size (Microns)	Cumulative Weight Percent
66	23.0
52	58.0
41	80.0
33	81.0
26	87.0
21	93.0
17	96.5
15	96.7
13	97.0
10	98.6
8	99.0
6	100.0

Note: Powder obtained from the Titanium Division of the National Lead Corporation.

Coatings were applied to both AISI-310 stainless steel and columbium-1 percent zirconium tubes, and some of the coating material from one of the AISI-310 stainless steel tubes was analyzed after plasma spraying. The only crystalline phase detected was $CaTiO_3$. The spectrographic analyses showed trace amounts of silicon and magnesium plus slight amounts of iron, chromium, and nickel. The presence of iron, chromium, and nickel is attributed to small amounts of the stainless steel substrate being present in the sample because of the scraping operation used in obtaining powder for analysis.

The coated stainless-steel tube was tested for 265 hours at 1350°F. The total hemispherical emittance data obtained during the first part of the test was 0.88. The emittance increased to 0.89 after 200 hours and maintained this value for the final 65 hours. Thermal cycling tests were performed after initial heating, after 100 hours, and after 200 hours. Visual examination of the specimen after testing showed no change in the coating texture or any indications of cracking or spalling. Examination of the cold test chamber surfaces showed no evidence of coating vaporization.

The coated columbium-1 percent zirconium tube was tested for 100 hours at 1350°F and for 68 hours at 1650°F. The emittance was 0.88 during the 100-hour test at 1350°F. However, when the temperature was increased to 1650°F, the emittance decreased to 0.62. The drop in emittance is attributed to a chemical breakdown of the coating. The columbium-1 percent zirconium tube was analyzed, and a substantial amount of oxygen was found. The oxygen content found by vacuum fusion testing was about 3200 ppm, whereas the amount expected in untested columbium-1 percent zirconium is less than 300 ppm.

Adherence testing was performed for coated AISI-310 stainless steel specimens. No adherence tests were performed for the coated columbium-1 percent zirconium specimens in view of the poor emittance results obtained with these specimens. The results of the fatigue tests for calcium-titanate-coated AISI-310 stainless steel are shown in Figure 28. As shown, the run-out stress level was about 55,000 psi, the same as for the uncoated material. No spalling or cracking of the coating occurred, and inspection at 1500°F of a specimen which withstood 10^7 cycles at 57,000 psi without failure revealed no coating separation (see Figure 29).
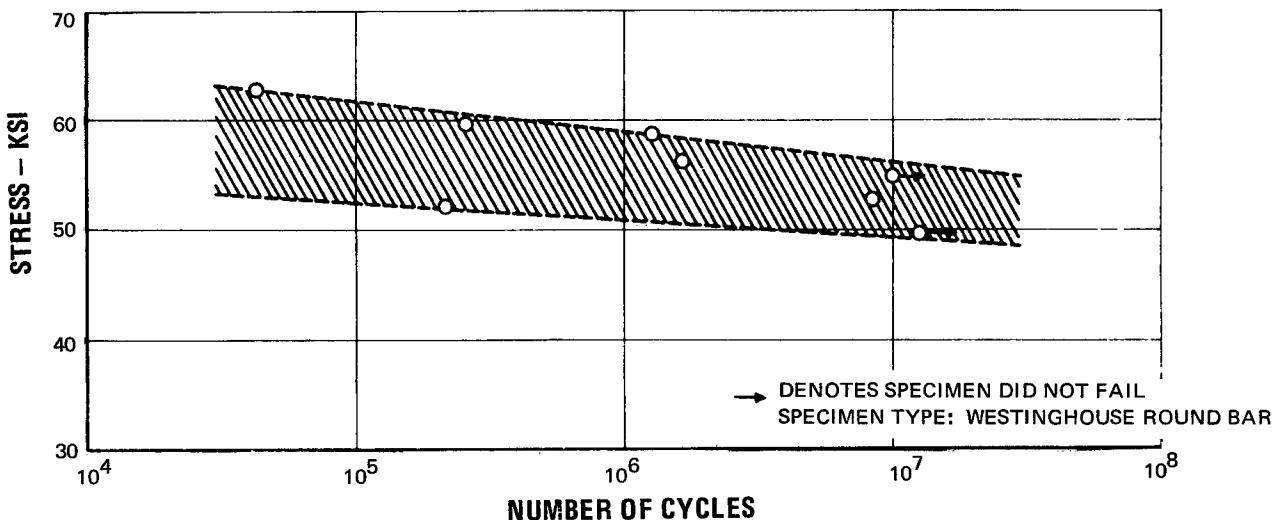

Figure 28   Fatigue Test Results Obtained at Room Temperature for AISI-310 Stainless Steel Coated With Calcium Titanate
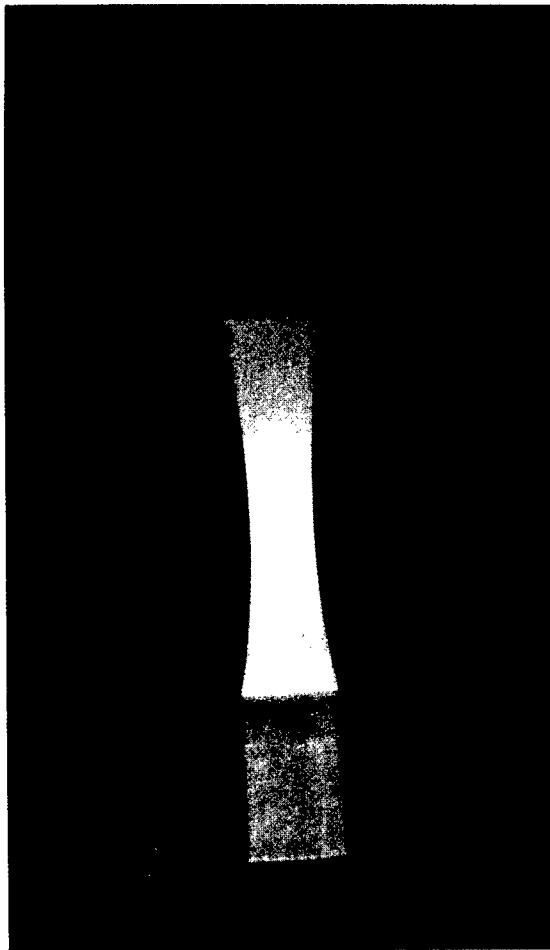
Figure 29   AISI-310 Stainless Steel Fatigue Specimen Coated With Calcium
Titanate and Heated to 1500°F for Coating Separation Inspection

On the basis of the emittance and adherence test results, calcium-titanate-
coated AISI-310 stainless steel was selected for long-term emittance testing,
and calcium-titanate-coated columbium-1 percent zirconium was rejected for
long-term emittance testing.

3. Zirconium Diboride-Molybdenum Disilicide

The zirconium diboride-molybdenum disilicide tested was obtained under the trade name "Boride Z." The material is 87 weight percent zirconium diboride (ZrB_2) and 13 weight percent molybdenum disilicide ($MoSi_2$) in solid solution.

The material was crushed and screened to a -250 +325 mesh size and plasma sprayed onto a columbium-1 percent zirconium tube to a thickness of 4 mils. Emittance testing, however, indicated that the emittance of this material is under 0.85, which is the minimum acceptable value for long-term testing. In addition, problems were encountered in obtaining an adequate bond between the coating and the substrate. Consequently, this material was rejected for long-term emittance testing.

4. Aluminum Oxide-Aluminum Titanate

An aluminum oxide-aluminum titanate composition was obtained from the Zirconium Corporation of America. This composition was prepared from 88 weight percent aluminum oxide and 12 weight percent titanium oxide. Emission spectrographic analysis detected 0.5 percent iron, 0.1 percent silicon, 0.6 percent magnesium, and a trace of manganese. The particle size distribution of the material as determined by screen analysis is shown in Table XVI.

TABLE XVI

PARTICLE SIZE DISTRIBUTION OF ALUMINUM
OXIDE-ALUMINUM TITANATE POWDER

Particle Size (Microns)	Cumulative Weight Percent
63	0
50	17.0
40	71.0
32	100.0

Note: Powder obtained from the Zirconium Corporation of America.

Several columbium-1 percent zirconium tubes were plasma sprayed with the aluminum oxide-aluminum titanate material. Analysis of scrapings from the tube after spraying indicated the presence of the same constituents as before spraying in essentially the same percentages.

One of the specimens was tested for 268 hours at 1700°F in a vacuum of not less than 1×10^{-8} torr. The emittance was about 0.85 throughout the test. After testing, the coating texture was unchanged, and visual examination of the cold test chamber surfaces revealed no indication of coating vaporization.

The emittance during this test appeared to be stable at a level, above the minimum acceptable level, and, therefore, columbium-1 percent zirconium coated with aluminum oxide-aluminum titanate was selected for long-term emittance testing.

5. Stabilized Titanium Oxide Composition

A proprietary stabilized titanium oxide composition designated as Y692 was obtained from the Zirconium Corporation of America. Emission spectrographic analysis of the material detected the presence of 0.01 percent magnesium, 0.02 percent silicon, 0.01 percent iron, and trace amounts of aluminum, copper, and nickel. The particle size distribution of the material as determined by screen analysis is shown in Table XVII.

TABLE XVII

PARTICLE SIZE DISTRIBUTION OF STABILIZED
TITANIUM OXIDE COMPOSITION

Particle Size (Microns)	Cumulative Weight Percent
63	36.0
50	55.0
40	75.0
32	99.0
25	100.0

Note: Powder obtained from the Zirconium Corporation of America.

Specimens were prepared by plasma-arc spraying columbium-1 percent zirconium tubes with 4-mil-thick layers of the material. Analysis of the coating after spraying detected the presence of 0.02 percent silicon, 0.3 percent aluminum, and trace amounts of iron, magnesium and manganese.

Two specimens were subjected to emittance testing. The first specimen was tested for 294 hours at 1700°F in a vacuum of 1×10^{-8} torr. The emittance throughout the test was about 0.87. The specimen was thermally cycled after initial heating and after 100 and 250 hours of testing. Examination of the specimen after testing detected no cracking, spalling, or other visible changes in the coating, nor did visual examination of the cold test chamber surfaces reveal any evidence of coating vaporization.

Although the first test indicated that the coating was suitable for long-term testing, a second test was conducted to verify the results since this material had not been tested previously. During the second test, the emittance again was 0.87. The specimen was thermally cycled after initial heating and after 100 and 240 hours of testing. In addition, a malfunction of the voltage regulator caused the specimen to be overheated by 250°F for two hours after 260 hours of testing. No adverse effects were visible.

In view of these results, this coating-substrate combination was selected for long-term testing, and the specimen which had been tested for 294 hours was installed in one of the long-term emittance test chambers. However, after a very short period, localized coating separation occurred, and the emittance dropped to about 0.80. The areas of separation appeared darker than the adjacent areas, as shown in Figure 30.
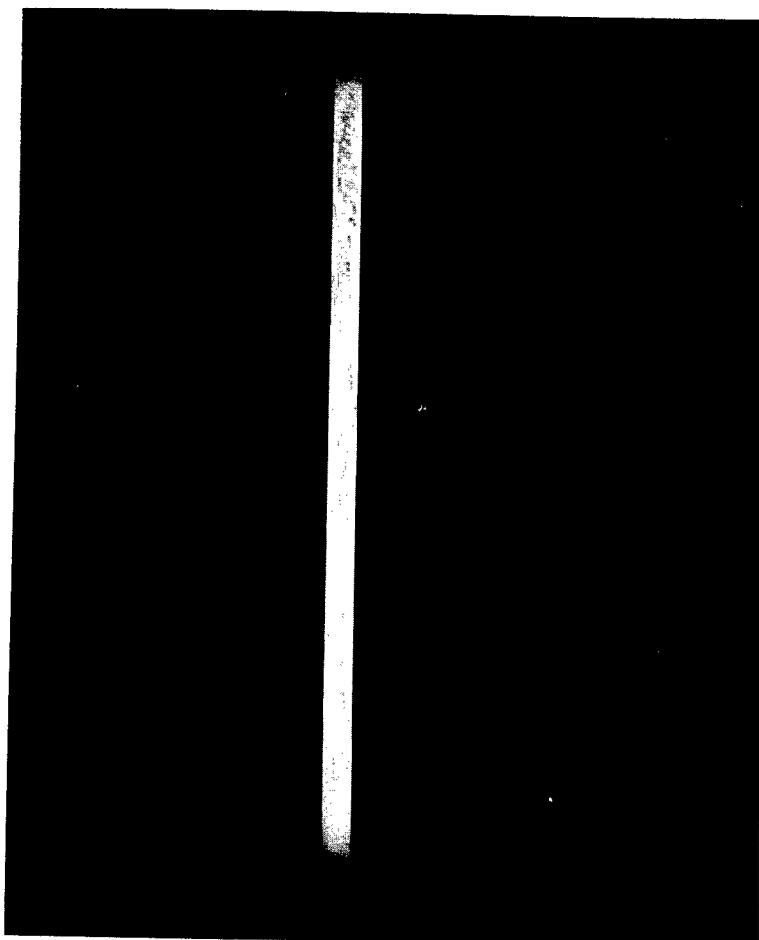
Figure 30   Appearance of Columbium-1 Percent Zirconium Tube Coated With Stabilized Titanium Oxide Composition After 50 Hours of Long-Term Testing at 1700°F

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In order to determine if the coating separation was a characteristic of the coating material or only a peculiarity of the particular specimen, a second specimen which had not been subjected to short-term testing was installed in a long-term emittance test chamber and tested at 1700°F in a vacuum of 1×10^{-8} torr. For the first 300 hours, the emittance remained between 0.86 and 0.87, but after 300 hours, evidence of coating separation was observed, and the emittance decreased. The test was continued for another 700 hours to determine the amount of separation that would occur and its effect on the emittance. At the end of this period, extensive separation had occurred, and the emittance had dropped to 0.78.

Since coating separation had occurred on both specimens after about 300 hours of testing, this material was rejected as unsuitable for space radiator use at 1700°F.

6. Zirconium Titanate

Zirconium titanate powder was obtained from the Zirconium Corporation of America. X-ray diffraction analysis indicated that $ZrTiO_4$ was the only phase present, and spectrographic analysis detected the presence of 0.3 percent silicon, 0.01 percent magnesium, 0.3 percent aluminum, 0.6 percent hafnium, and traces of iron and manganese. The particle size distribution of the powder as determined by screen analysis, is shown in Table XVIII.

TABLE XVIII

PARTICLE SIZE DISTRIBUTION OF
ZIRCONIUM TITANATE POWDER

Particle Size (Microns)	Cumulative Weight Percent
63	32.0
50	84.0
40	93.0
32	95.0
25	96.0
20	99.0
17	100.0

Note: Powder obtained from the Zirconium Corporation of America.

Several specimens were prepared by plasma-arc spraying 4-mil thick coatings of zirconium titanate on columbium-1 percent zirconium. Scrapings from the tube were analyzed by X-ray diffraction and spectrographic analysis. X-ray diffraction analysis indicated that zirconium titanate was the only phase present, and spectrographic analysis detected the presence of 0.07 percent silicon, 0.2 percent aluminum, 1.0 percent hafnium, and traces of iron, magnesium, and manganese.

One of the specimens was tested at 1700°F in a vacuum of 1×10^{-8} torr for 312 hours. Initially, the emittance level was acceptable at 0.85, but it gradually dropped to 0.82 by the end of the 312 hours. Consequently, since the emittance dropped below the minimum acceptable level, this coating material was rejected for long-term emittance testing.

7. Barium Titanate Composition

A composition containing 88 weight percent barium titanate, 9.4 weight percent barium zirconate, and 2.6 weight percent manganese dioxide was obtained from the Zirconium Corporation of America. X-ray diffraction analysis detected only the major constituent, barium titanate. Spectrographic analysis revealed the presence of 0.04 percent silicon, 0.02 percent magnesium, 0.1 percent aluminum, 0.05 percent hafnium, and a trace of iron. The particle size distribution of the powder as determined by screen analysis is shown in Table XIX.

TABLE XIX

PARTICLE SIZE DISTRIBUTION OF BARIUM
TITANATE COMPOSITION

Particle Size (Microns)	Cumulative Weight Percent
63	0
50	25.0
40	42.0
32	52.0
25	65.0
20	76.0
17	85.0
14	91.0
12	95.0
9	98.0
7	99.0
6	100.0

Note: Powder obtained from the Zirconium Corporation of America.

Specimens for emittance testing were prepared by plasma-arc spraying 4-mil thick coatings on columbium-1 percent zirconium tubes. Following spraying, scrapings of the coating were analyzed. As before spraying, X-ray diffraction analysis detected only barium titanate. Spectrographic analysis showed the presence of 0.02 percent silicon, 0.1 percent aluminum, 0.1 percent hafnium, and traces of iron and manganese.

One of the specimens was tested at 1700°F in a vacuum of 1×10^{-9} torr. Initially, the emittance was 0.80, but it dropped to 0.71 after 97 hours of testing, and the test was terminated. The emittance of this coating was too low to warrant additional testing.

E. LONG-TERM EMITTANCE TESTING AND ANALYSIS

Four specimens were selected for long-term emittance testing on the basis of the preliminary screening tests. These were calcium-titanate-coated AISI-310 stainless steel, iron-titanate-coated AISI-310 stainless steel, iron-titanate-coated columbium-1 percent zirconium, and columbium-1 percent zirconium coated with aluminum oxide aluminum titanate.

Testing involved heating the specimens in vacuum to 1350°F or 1700°F for 10,000 or 20,000 hours, depending on the substrate material. All specimens were thermally cycled to room temperature once each week. The cooling rates for the specimens are shown in Figures 31 and 32.
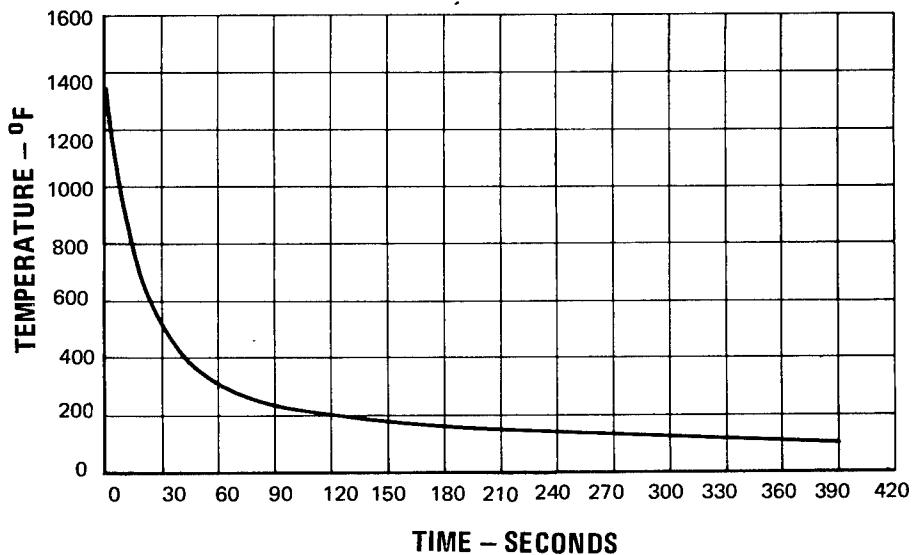
Figure 31   Thermal Shock Cooling Rate for Emittance Specimens Tested at 1350°F
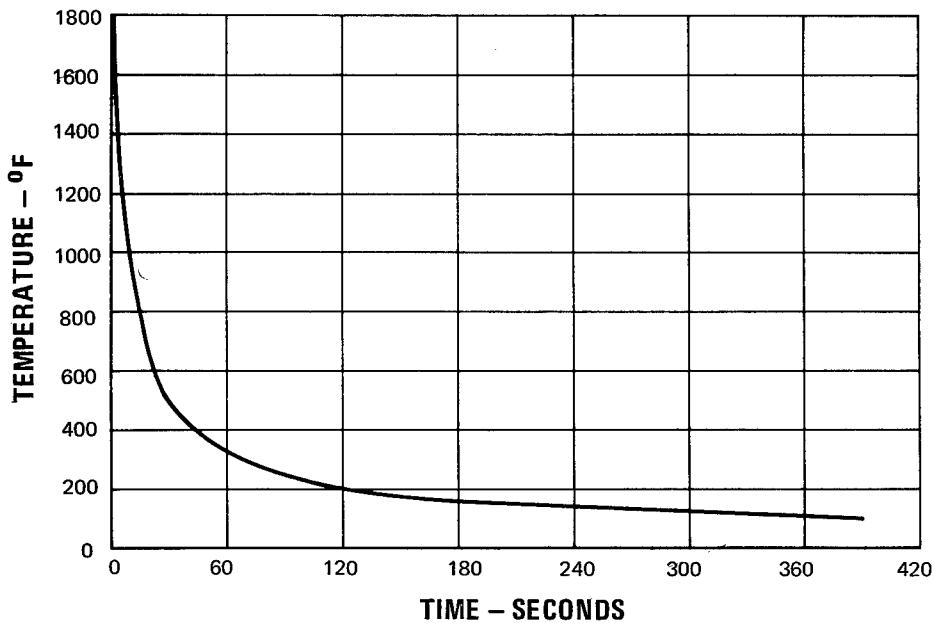
Figure 32   Thermal Shock Cooling Rate for Emittance Specimens Tested at
1700°F

1.   Calcium Titanate on AISI-310 Stainless Steel

The calcium-titanate-coated AISI-310 stainless steel specimen was tested for
20,000 hours in vacuum at 1350°F. The specimen was thermally cycled a total
of 112 times during the 20,000-hour period with no apparent adverse effects on
the emittance or adherence of the coating. The appearance of the specimen at
1350°F shortly before termination of the test is shown in Figure 33.

The emittance of the specimen was excellent throughout the test. As shown in
Figure 34, the emittance was 0.91 at the beginning of the test, decreased
gradually to 0.88 after 13,000 hours, and remained steady at about 0.88 for
the final 7,000 hours. The vacuum maintained in the test chamber during the
test was better than 1×10^{-7} torr except for a brief period near the end of the
test.

Examination of the specimen following the test revealed a slight darkening of
the coating, but no change in texture was apparent, nor was there any indication
of cracking or spalling. Attempts to mechanically remove the coating with a
silicon-carbide scraping tool indicated that the coating was extremely well
bonded to the substrate. The appearance of the specimen at room temperature
after the test is shown in Figure 35.
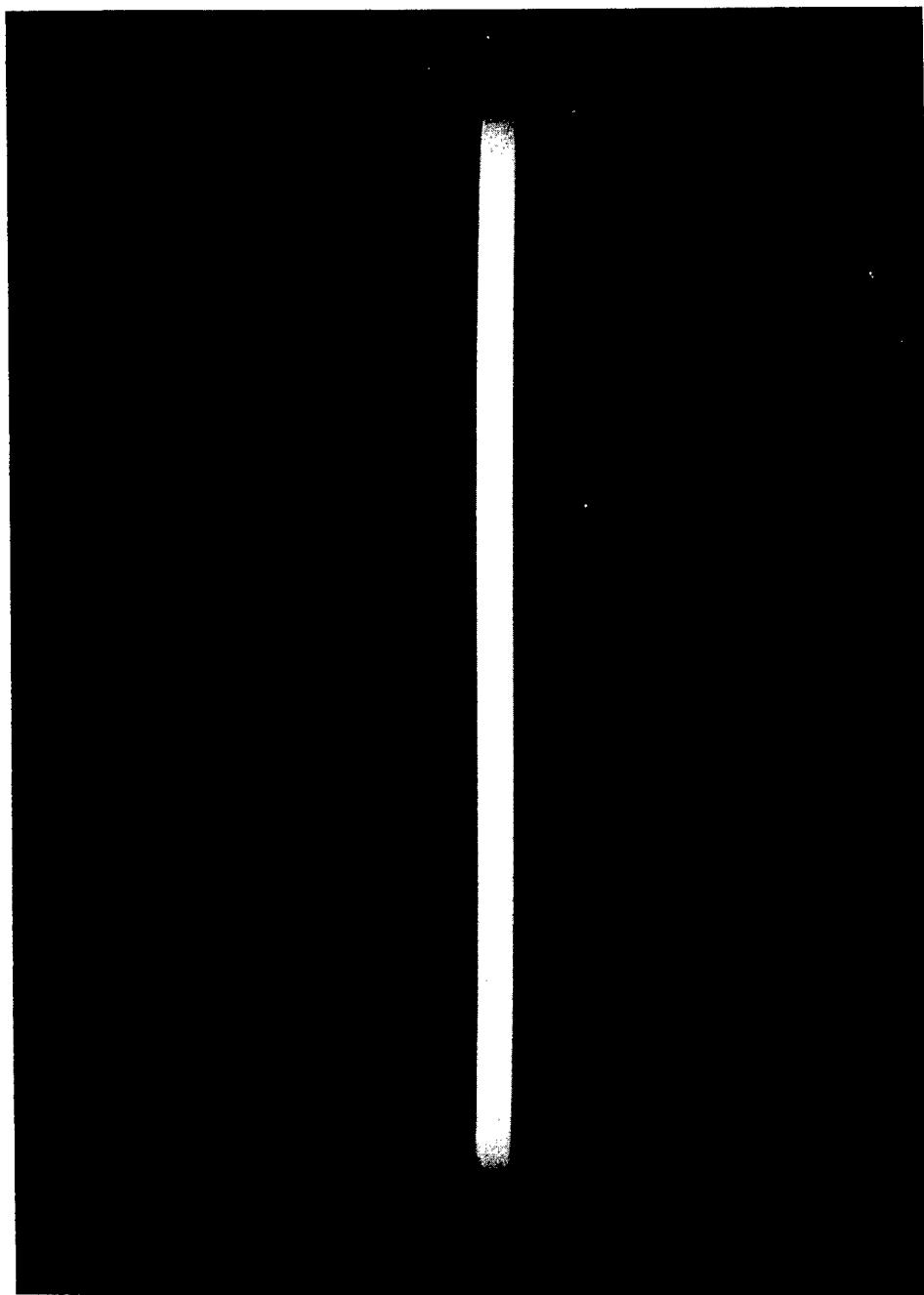
Mag: 0.9X

Figure 33   Appearance of Calcium-Titanate-Coated AISI-310 Stainless Steel
Tube at 1350°F After 20,000 Hours of Testing

X-23808
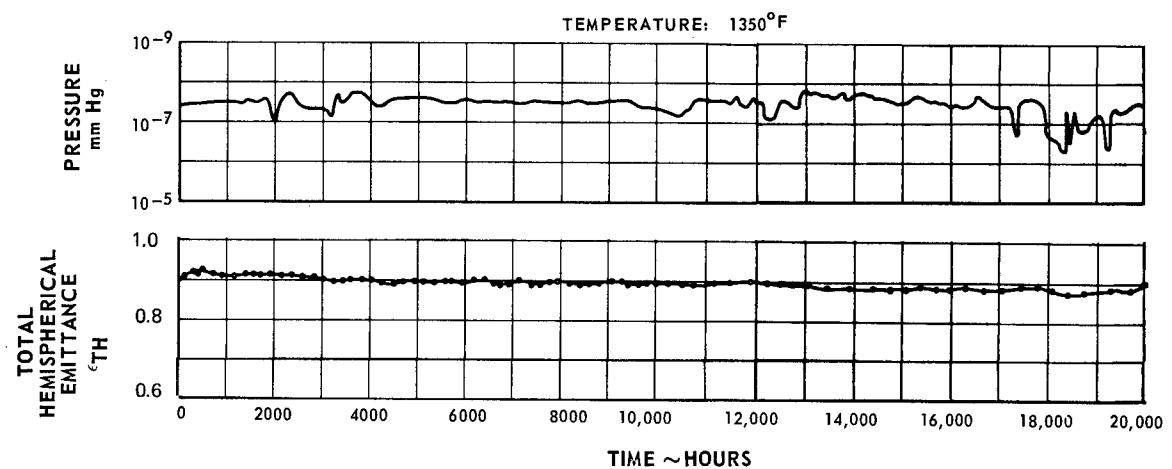
Figure 34   Pressure and Total Hemispherical Emittance for Long-Term Endurance Test of **Calcium-Titanate-Coated** AISI-310 Stainless Steel
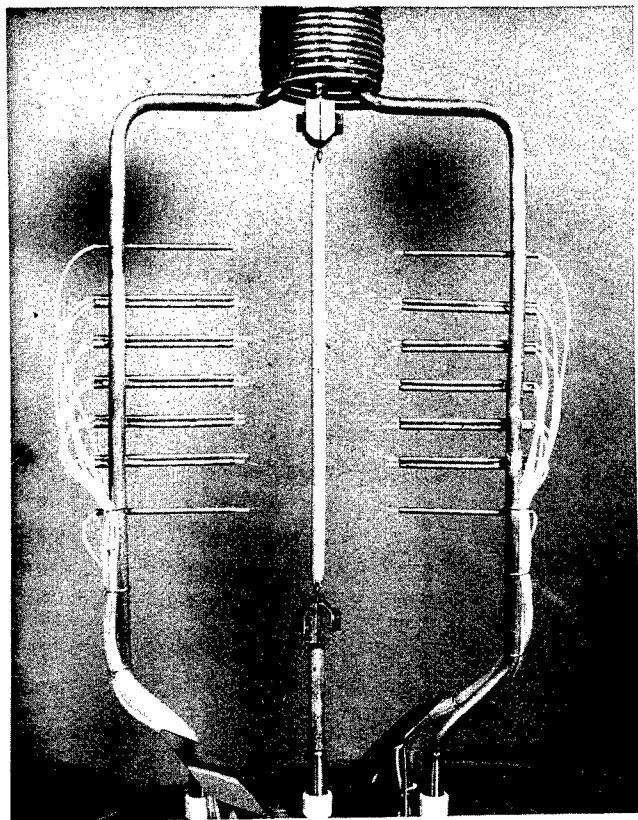
Mag: 0.6X

Figure 35   Appearance of Calcium-Titanate-Coated AISI-310 Stainless Steel Tube at Room Temperature After 20,000 Hours of Testing   X-23949

Semiquantitative spectrographic analyses were made on the coating both immed-
iately after application and after endurance testing. These results are shown
in Table XX.

TABLE XX

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF CALCIUM-TITANATE ON AISI-310
STAINLESS STEEL TUBE

| | Impurity Content (Weight Percent) | | | | | | |
	Fe	Cr	Ni	Al	Mn	Cu	Si	Mg
As Sprayed	0.2*	0.1*	0.07*	–	0.01	<0.01	<0.01	<0.01
After Test	–	0.1	–	0.01	0.5	<0.01	0.05	<0.01

* Presence of these constituents is attributed to small quantities of stainless
steel introduced when coating was scraped from substrate.

X-ray diffraction analysis of the coating in the as-sprayed condition and after
testing detected calcium titanate as the only crystalline phase present in both
cases.

The tested specimen and a sample of the substrate tubing in the as-received
condition were sectioned for metallographic examination. The structure found
in the as-received sample (Figure 36) is considered to be normal for annealed
AISI-310 stainless steel. The microstructure of the tested specimen, as shown
in Figure 37, contains substantial amounts of precipitates in an austenitic matrix.
Identification of the precipitated phases was attempted by metallographic tech-
niques. The results indicated that the more massive of the two distinguishable
phases in the matrix was sigma phase and that the smaller, more finely divided
phases were carbides.
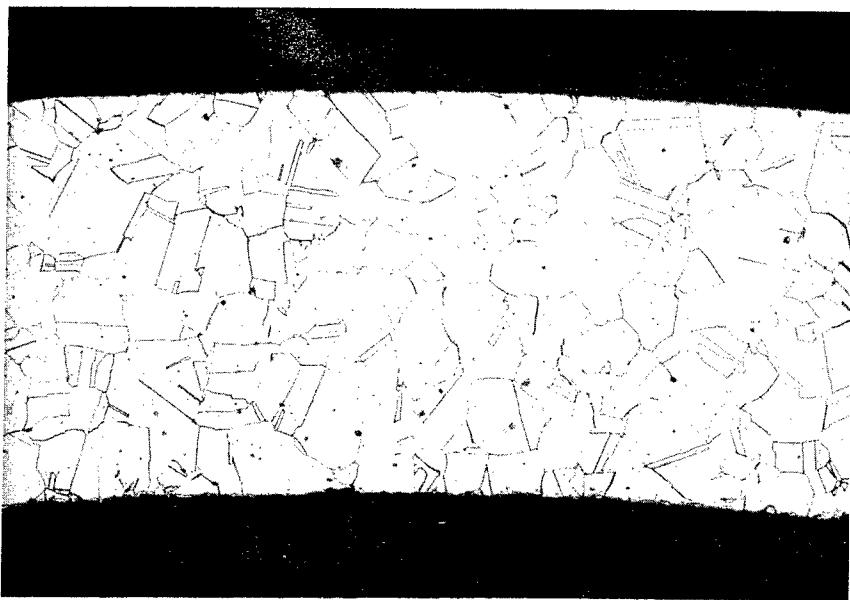
Etchant: 43% Glycerine, 43% HCL, 14% HNO$_3$ Mag: 200X

Figure 36   Photomicrograph of AISI-310 Stainless Steel Tube in the As-Received
             Condition
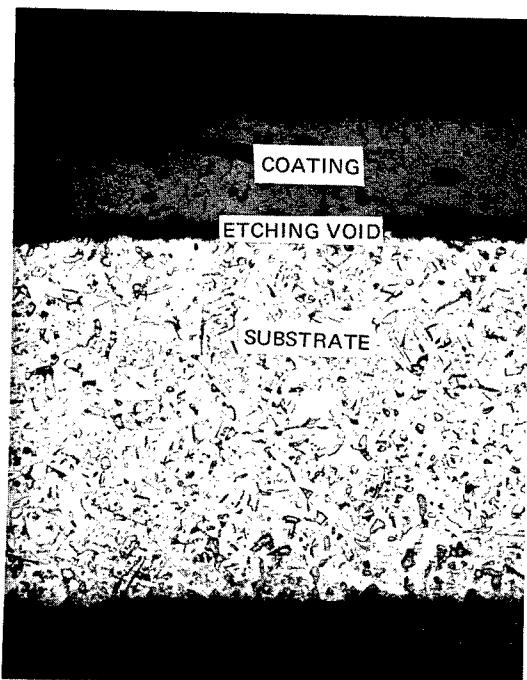
Mag: 200X   Mag: 500X
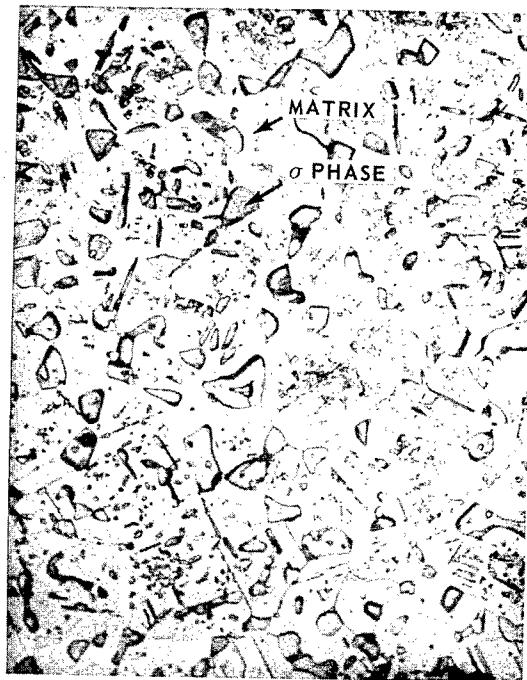
Etchant: 43% Glycerine, 43% HCL, 14% HNO$_3$

Figure 37   Photomicrographs of AISI-310 Stainless Steel Tube Coated With
             Calcium Titanate and Tested for 20,000 Hours at 1350°F

The photomicrographs shown in Figure 37 were etched to reveal the precipitates, but the etchant removed material from the interface between the coating and the substrate, making it appear that separation had occurred. The fact that no separation did occur is evident in the unetched photmicrograph shown in Figure 38.
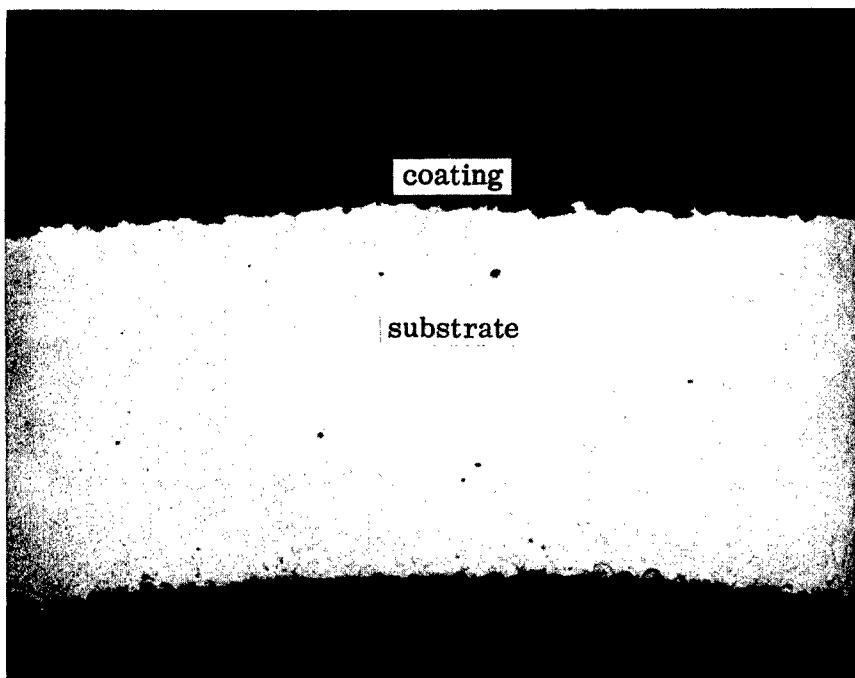
Mag: 200X

Figure 38   Unetched Photomicrograph of AISI-310 Stainless Steel Tube
             Coated With Calcium Titanate and Tested for 20,000 Hours at 1350°F

Microhardness traverses were made on the cross section of the stainless steel tube in the as-received condition and on the substrate after testing. Measurements were made with a Reichert microhardness tester using a load of 43 grams. The tube in the as-received condition had a diamond pyramid hardness of about 200 kg/mm^2, indicating that the material was fully annealed. This hardness was uniform throughout the cross section. The diamond pyramid hardness of the endurance-tested tube was about 245 kg/mm^2, with no significant variations measured throughout the cross section. These results are shown in Table XXI.

TABLE XXI

MICROHARDNESS TRAVERSE RESULTS FOR ENDURANCE
TESTED AISI-310 STAINLESS STEEL TUBE
COATED WITH CALCIUM TITANATE

Depth Below Interface (Mils)	Diamond Pyramid Hardness (kg/mm^2)	
	Traverse 1	Traverse 2
0.75	239	244
2.0	244	-
2.5	248	235
4.25	244	235
6.0	239	248
7.5	244	253
9.5	239	239

Note: Total wall thickness equals 10 mils.

In order to obtain more information concerning the changes which occurred in
the substrate of the tested specimen and also to determine whether any coating-
substrate interactions occurred, electron-beam microprobe analyses were
conducted on both an untested substrate and the tested substrate. The analyses
were performed with a Norelco electron probe microanalyzer.

Initially, electron microprobe and wet chemical analyses were performed on
the stainless steel tube in the as-received condition. The results of the two
analyses, shown in Table XXII, were in reasonable agreement and indicated
that the material conformed to the specifications established for the alloy.

TABLE XXII

COMPOSITION OF AISI-310 STAINLESS STEEL
TUBE IN AS-RECEIVED CONDITION

	Nominal		Wet Chemical Analysis	Electron Microprobe Analysis
	Minimum	Maximum		
Carbon	0	0.25	0.08	-
Manganese	0	2.00	1.85	1.0
Silicon	0	0.75	0.64	0.7
Phosphorus	0	0.040	-	0.1
Sulfur	0	0.030	-	0.1
Chromium	24.00	26.00	25.19	24.9
Nickel	19.00	22.00	19.50	20.2
Molybdenum	0	0.50	0.20	-
Copper	0	0.50	-	-
Iron	Balance	Balance	Balance	51.4

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The relative X-ray line scan intensities for iron and chromium across the stainless steel in the as-received condition indicated that the material was homogeneous (Figure 39).
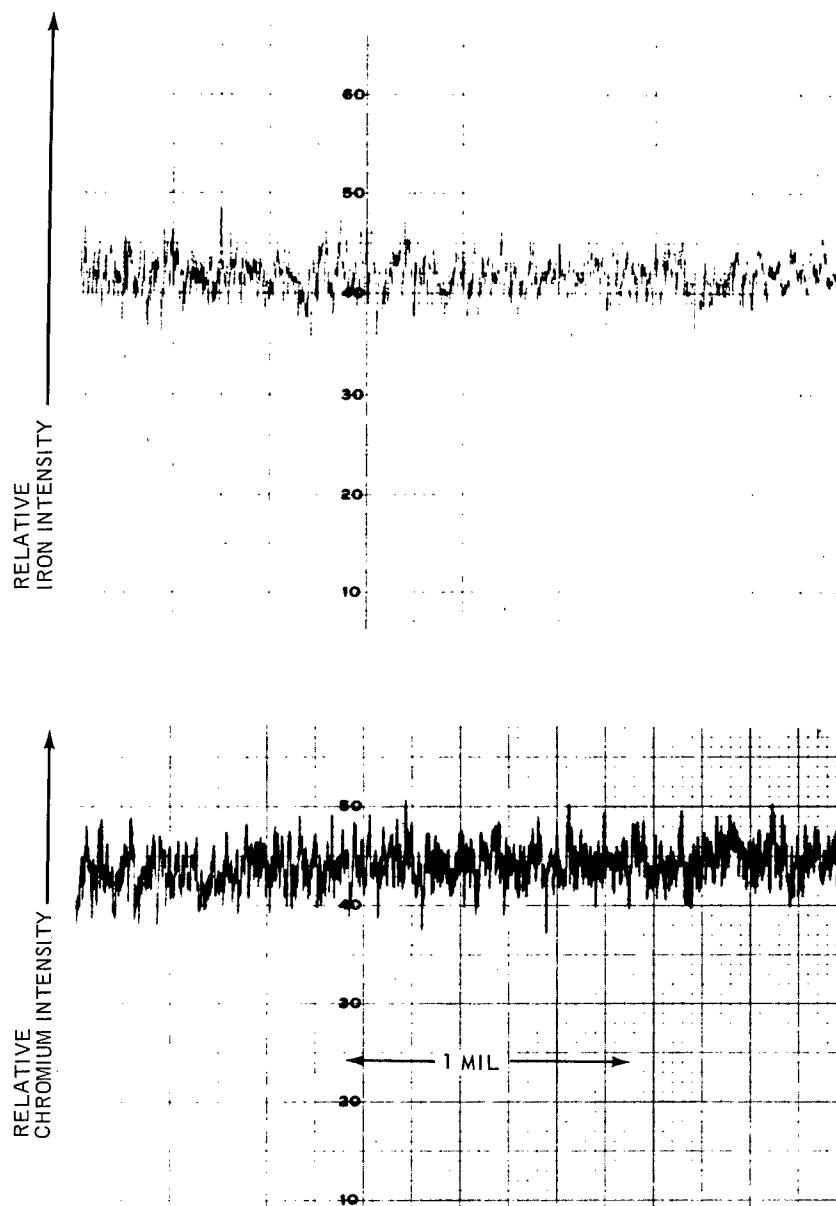
Figure 39   Relative X-ray Line Scan Intensities for Iron and Chromium in AISI-310 Stainless Steel Specimen in As-Received Condition

The scan of the tested tube, as shown in Figure 40, reveals a considerable variation in both iron and chrome levels as a function of position within the substrate. The regions which showed higher-than-average chrome and lower-than-average chrome and lower-than-average iron are believed to be zones in which the electron beam impinged on the massive precipitate.

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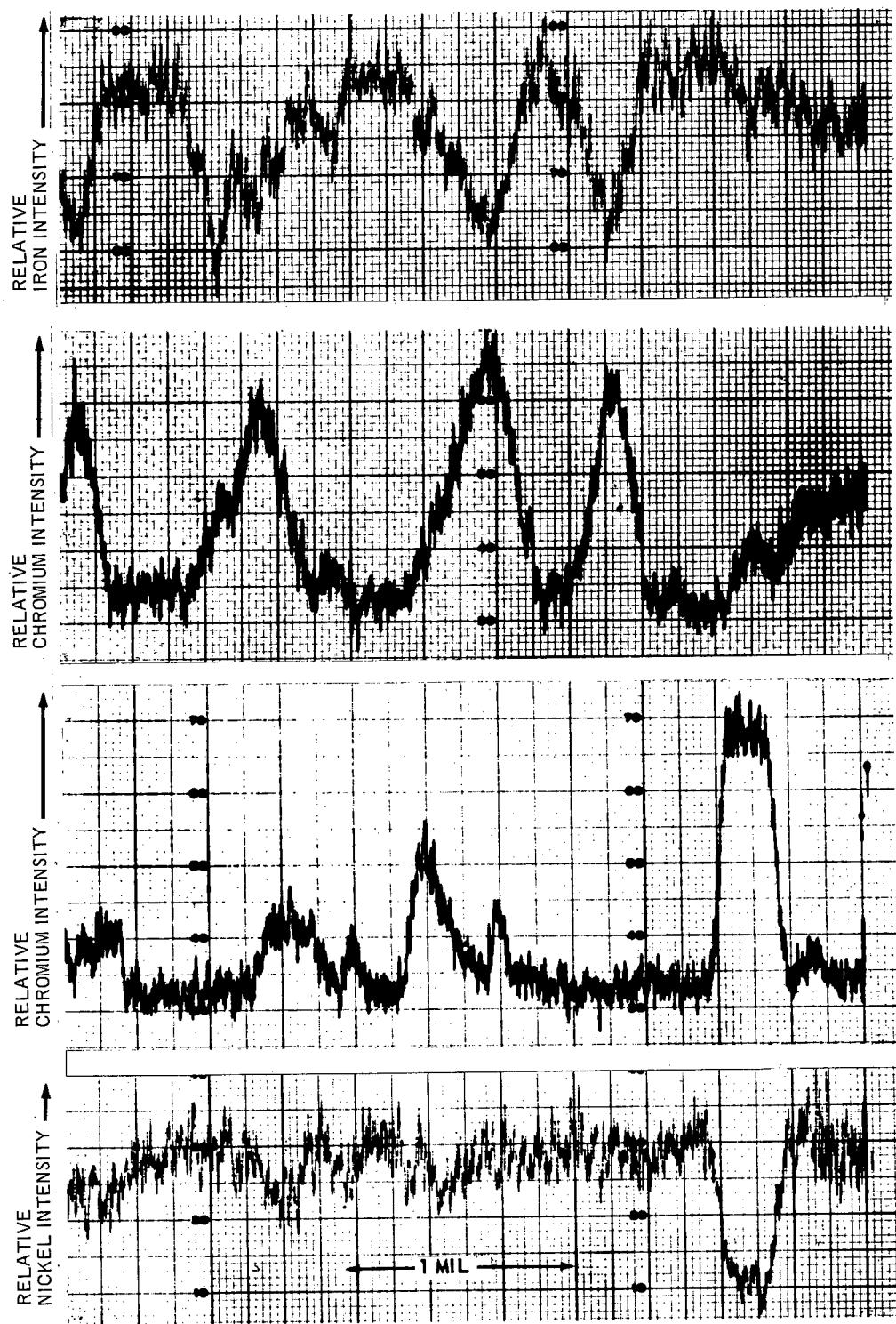
Figure 40 Typical Relative X-ray Line Scan Intensities for Iron and Chromium
and for Nickel and Chromium in AISI-310 Stainless Steel Specimen
Coated With Calcium Titanate and Tested for 20,000 Hours at 1350°F

Quantitative point-count analyses (concentrations of specific elements at specific points in the sample) were performed to determine the composition of the phases formed during the endurance test. The results, shown in Table XXIII, indicate that the more massive phase falls into the sigma phase composition, as indicated previously in the metallurgical examination section. The austenitic matrix material had a higher iron and nickel content and a lower chromium content than the sigma phase. The overall composition in the tested specimen was essentially the same as that of the specimen in the as-received condition, indicating no preferential loss of significant quantities of material during testing.

TABLE XXIII

COMPOSITION OF AISI-310 STAINLESS STEEL COATED
WITH CALCIUM TITANATE AND TESTED
FOR 20,000 HOURS AT 1350°F

| | Concentration (Weight Percent) | | | | |
	Cr	Ni	Mn	Fe	Si
Sigma Phase	42.1	9.1	0.8	45.4	1.1
Matrix	18.8	21.7	1.7	55.7	0.6
Overall Composition	24.7	20.4	1.1	51.5	0.8

The substrate was examined for evidence of titanium diffusion by quantitative point-count analysis, and the results are shown in Table XXIV. As shown, the titanium concentration decreased from 0.07 weight percent at the substrate surface to less than 0.01 weight percent at a depth of 1.5 mils, indicating that only a very limited amount of titanium diffusion occurred during the test.

The results shown in Table XXIV were verified by scanning across the coating-substrate interface and measuring the relative concentrations of titanium and iron. The results (see Figure 41) clearly demonstrate the absence of any significant interdiffusion of these elements.

TABLE XXIV

CONCENTRATION OF TITANIUM ACROSS AISI-310 STAINLESS
STEEL TUBE COATED WITH CALCIUM TITANATE
AND TESTED FOR 20,000 HOURS AT 1350°F

Depth Below Interface (Mils)	Concentration (Weight Percent)
0.25	0.07
0.75	0.02
1.50	<0.01
3.75	<0.01
7.0	<0.01

Note: Wall thickness equals 10 mils.
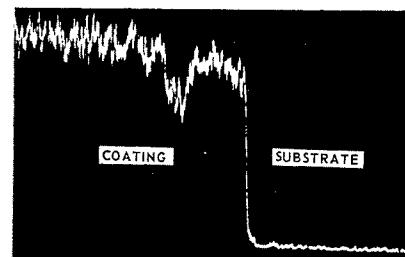
Relative Intensity for Titanium
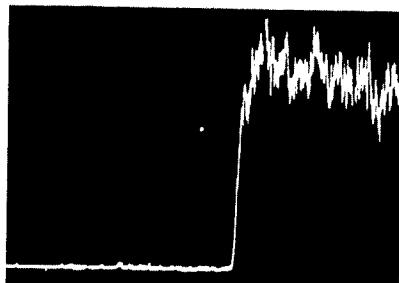
Relative Intensity for Iron
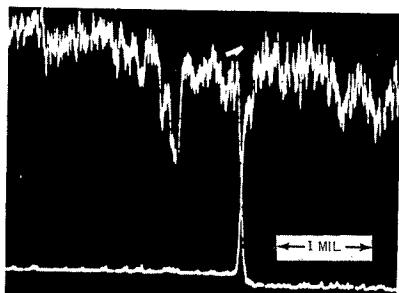
Composite Intensities for Iron and Titanium

Figure 41   Relative X-ray Line Scan Intensities for Iron and Titanium Across
the Interface of Calcium Titanate and AISI-310 Stainless Steel After
Testing for 20,000 Hours at 1350°F

A vacuum fusion analysis was performed on the substrate in the as-received condition and after testing. The oxygen content in the tube before and after testing was found to be 0.041 and 0.049 weight percent, respectively. The difference between the values is less than the experimental error of the aparatus. The analysis of the tested substrate was performed across the full section thickness after the coating had been mechanically removed and the surface had been cleaned by acid etching. Since there was no significant change in the oxygen content, the oxygen distribution across the substrate was not determined.

In summary, the calcium-titanate-coated AISI-310 stainless steel tube tested for 20,000 hours in vacuum at 1350°F demonstrated a stable emittance of about 0.89 and excellent bonding between the coating and the substrate. Only a very slight amount of interaction between the coating and the substrate occurred. In the substrate, a substantial amount of sigma and carbide phases precipitated. Prolonged exposure at 1350°F would have a tendency toward sigma phase formation as observed after 20,000 hours of testing. The formation of these precipitates in the substrate is not related in any way to the coating. The increase in the substrate hardness observed after testing is believed to have been caused by the presence of these precipitates, particularly the finely divided phase.

2. Iron Titanate on AISI-310 Stainless Steel

The AISI-310 stainless steel tube was tested for 20,000 hours in vacuum at 1350°F. The specimen was thermally cycled a total of 114 times during the test.

The emittance of the specimen was very stable throughout the test with only a slight decrease from 0.89 to 0.87 during the 20,000-hour period (see Figure 42). As shown in Figure 42, the vacuum maintained was about 2×10^{-8} torr.

Some coating separation occurred during the test, as shown in Figure 43. The start of separation at the ends of the specimen was most likely caused by crimping the ends of the tube for electrical connections. The emittance of the specimen was not affected by the separation at the ends of the tube since emittance measurements were made only for the central 1.5 inches of the tube. Separation around the black-body holes, which are in the test section, involved less than two percent of the test section area, and, therefore, had an insignificant effect on the measured emittance.
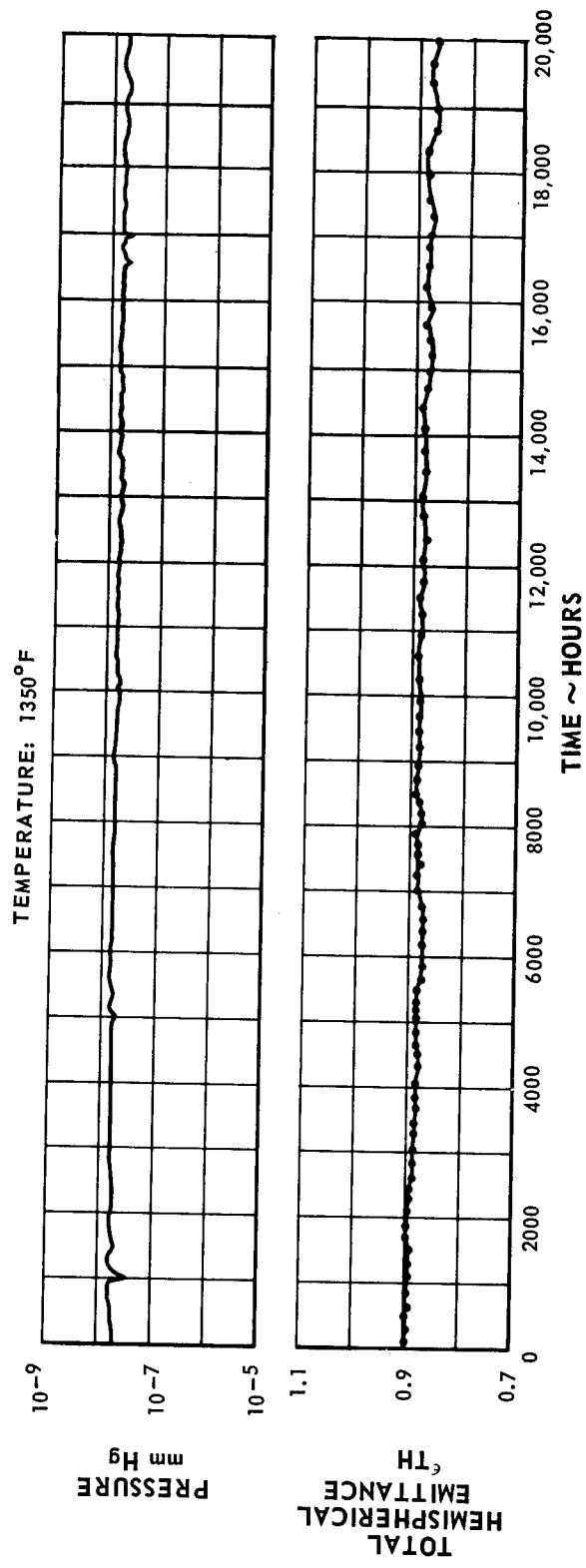
Figure 42   Pressure and Total Hemispherical Emittance for Long-Term Endurance Test of Iron-Titanate-Coated AISI-310 Stainless Steel
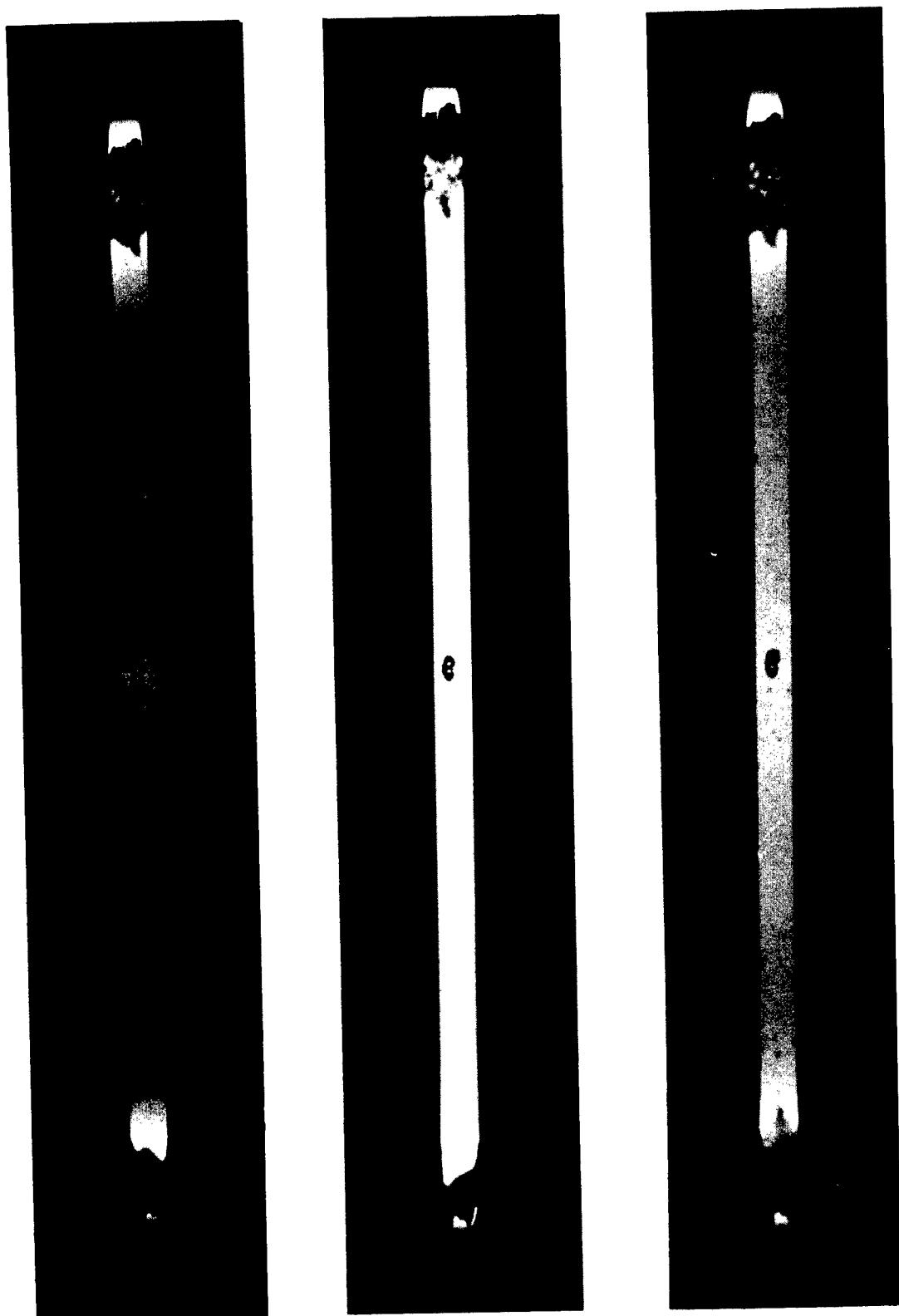
Mag: 0.75X

Figure 43   Appearance of Iron-Titanate-Coated AISI-310 Stainless Steel Tube at
1350°F After 15,400 Hours (Left), 17,500 Hours (Center), and 20,000
Hours (Right) Showing Progression of Coating Separation

XP-69336/XP-22281/X-24143

The appearance of the specimen at room temperature after completion of the test is shown in Figure 44. The texture and integrity of the coating was unchanged from that observed at the start of the test, and only a slight change in color occurred. The adherence of the coating to the substrate was good except at the ends of the specimen and in the vicinity of the black-body holes.
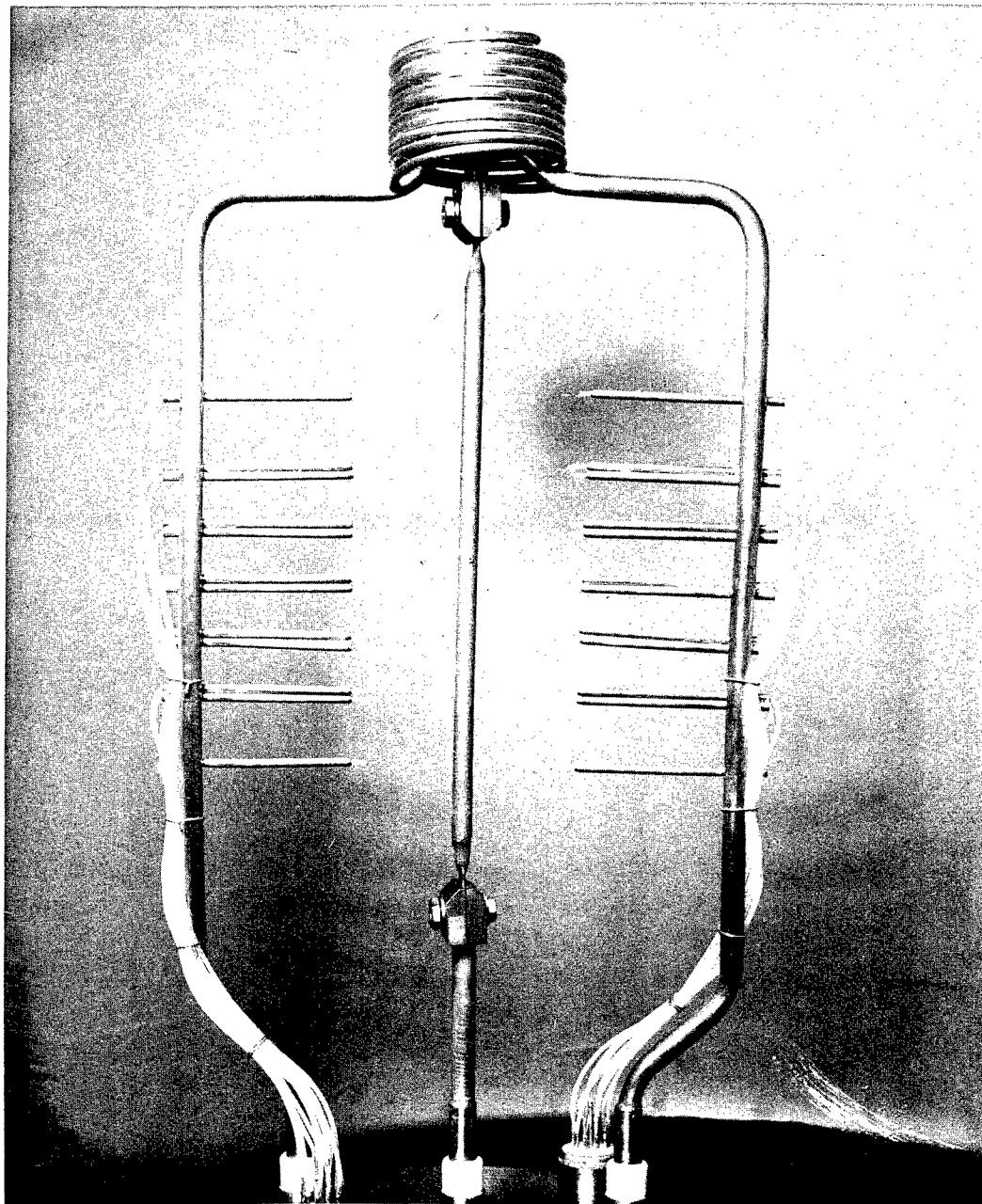
Mag: 0.4X

Figure 44   Appearance of Iron-Titanate Coated AISI-310 Stainless Steel Tube
at Room Temperature After 20,000 Hours of Testing   X-24139

The coating was subjected to semiquantitative spectrographic analysis before and after testing, and the results are shown in Table XXV. The changes which occurred were small and generally were within the accuracy limits of the analysis.

TABLE XXV

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF IRON TITANATE ON AISI-310
STAINLESS STEEL TUBE

| | Impurity Content (Weight Percent) | | | | | | |
	Al	Mn	Mg	Cr	Cr	Si	Ni
As Sprayed	0.7	0.5	0.01	0.1	0.05	0.3	0.04
After Test	0.5	1.0	0.01	0.5	0.2	0.5	

X-ray diffraction analysis of the coating indicated that testing did cause some changes in the structure of the coating. In the as-sprayed coating, the only crystalline phase detected was iron titanate. After testing, the major phase present in the material was iron titanate, but substantial amounts of titanium oxide and some ferrous oxide were also detected. The relative amounts of the various phases present were indicated by the intensities of the major peaks for these phases.

The endurance-tested coated specimen was sectioned for metallographic analysis. The etched photomicrograph (see Figure 45) shows that the substrate contained precipitates which were identical in appearance to those observed in the calcium-titanate-coated specimen. The slight difference in size and distribution of the precipitates in the substrate from those observed in the calcium-titanate-coated substrate is considered to be caused by normal variations in the precipitation reaction from section to section. An unetched photomicrograph is shown in Figure 46. As shown, no separation is evident between the coating and the substrate in this region.

Two microhardness traverses were made on a cross section of the endurance-tested tube. The average diamond pyramid hardness was about 210 kg/mm^2, which represents a 10 kg/mm^2 increase from the untested state. There were no significant variations across the tube wall. These results are shown in Table XXVI.
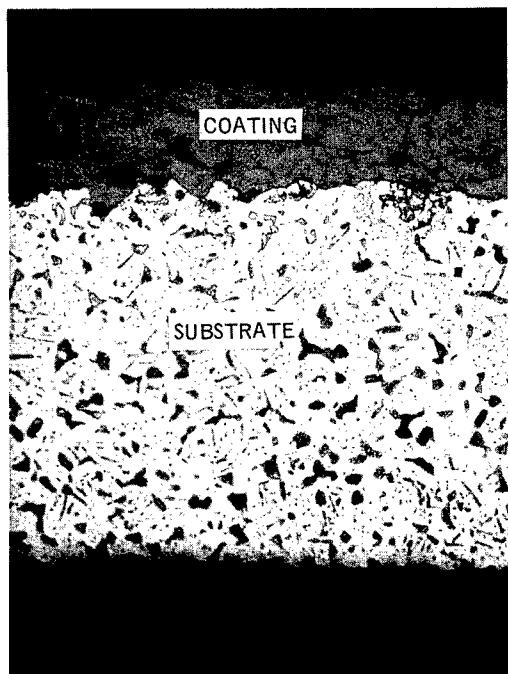
Mag: 200X

Mag: 500X

Etchant: 43% Glycerine, 43% HCL, 14% HNO₃

Figure 45   Photomicrographs of AISI-310 Stainless Steel Tube Coated With
            Iron Titanate and Tested for 20,000 Hours at 1350°F
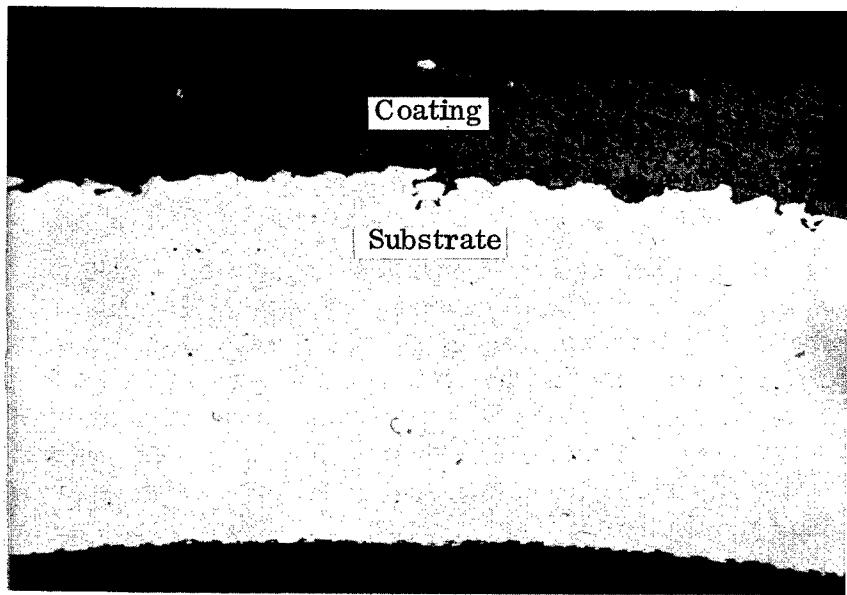
Mag: 200X

Figure 46   Unetched Photomicrograph of AISI-310 Stainless Steel Tube Coated
            With Iron Titanate and Tested for 20,000 Hours at 1350°F

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TABLE XXVI

MICROHARDNESS TRAVERSE RESULTS FOR ENDURANCE-
TESTED AISI-310 STAINLESS STEEL TUBE
COATED WITH IRON TITANATE

Depth Below Interface (Mils)	Diamond Pyramid Hardness (kg/mm^2)	
	Traverse 1	Traverse 2
0.5	211	211
2.0	208	-
2.5	-	219
3.5	215	-
3.75	-	215
5.5	208	-
6.0	-	208
7.0	208	-
7.5	-	211
9.0	211	208

Note: Total wall thickness equals 10 mils.

Electron microprobe analyses were conducted on the tested specimen to identify
the precipitates which formed in the austenitic matrix. Quantitative point count
analyses for iron and chromium were performed on the more massive precipitate,
and the results indicated that this precipitate was sigma phase. The results
were essentially identical to those obtained from the calcium-titanate-coated
tube. The relative concentrations of iron and chromium were determined
(see Figure 47), and, as for the calcium-titanate-coated specimen, it was found
that the concentration of iron varied inversely with that of chromium. Hence,
the changes which occurred in the iron-titanate-coated tubes were identical to
those which occurred in the calcium-titanate-coated tube.
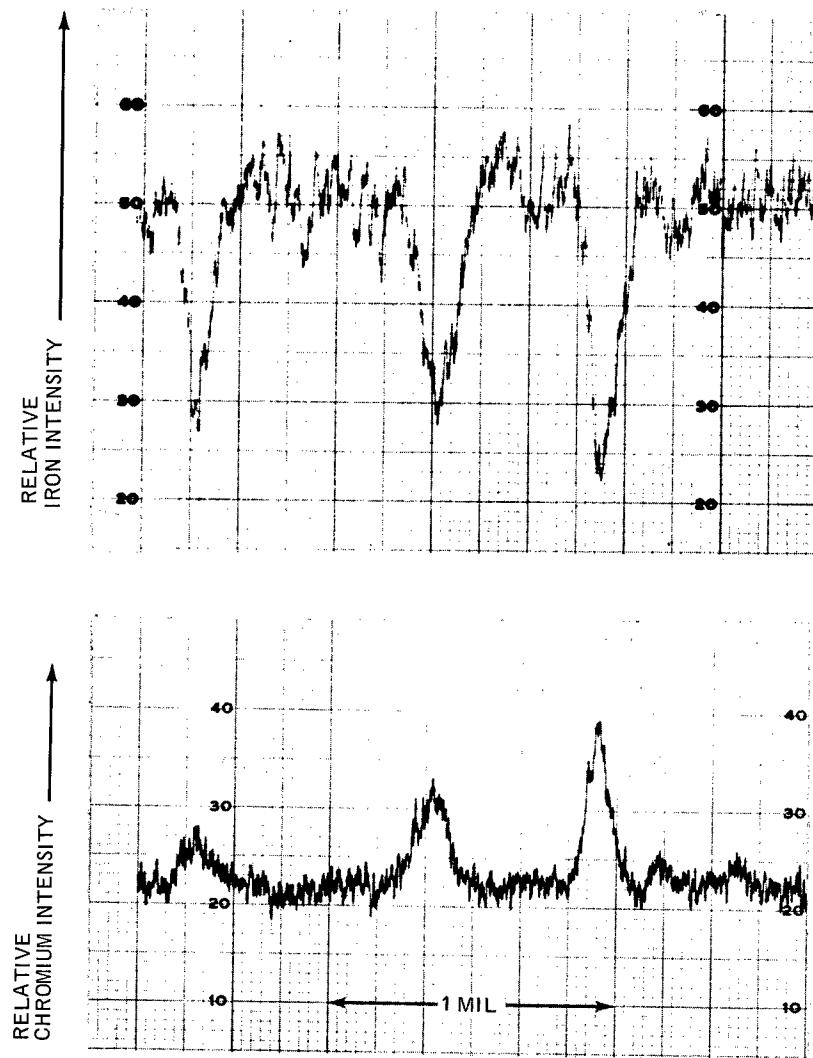
Figure 47   Relative X-ray Line Scan Intensities for Iron and Chromium in AISI-
310 Stainless Steel Specimen Coated With Iron Titanate and Tested
for 20,000 Hours at 1350°F

Quantitative point count analyses were performed at the coating-substrate
interface to determine whether any titanium diffused from the coating into the
substrate. As shown in Table XXVII, the titanium concentration was 0.06 weight
percent at the surface and diminished to less than the detectability limit of 0.01
weight percent at a depth of 1.25 mils. X-ray line scans for titanium and
chromium were made across the interface. These scans, shown in Figure 48,
detected no significant interdiffusion of these elements.

TABLE XXVII

CONCENTRATION OF TITANIUM ACROSS AISI-310 STAINLESS
STEEL TUBE COATED WITH IRON TITANATE AND
TESTED FOR 20,000 HOURS AT 1350°F

Depth Below Interface (Mils)	Concentration (Weight Percent)
0.25	0.06
0.75	0.02
1.25	<0.01
3.75	<0.01
6.75	<0.01

Note: Wall thickness equals 10 mils.
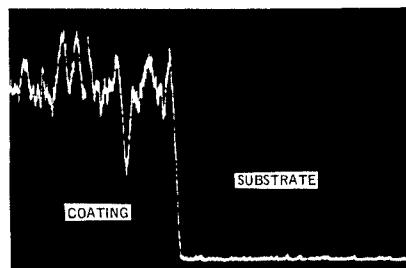
Relative Intensity for Titanium
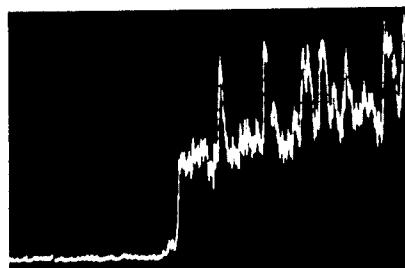
Relative Intensity for Chromium
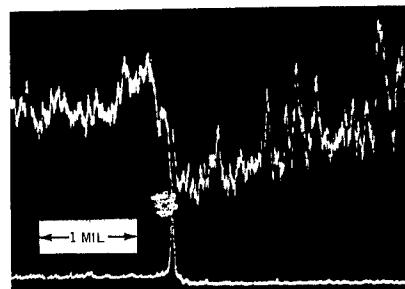
Composite Intensities for Titanium and Chromium

Figure 48 Relative X-ray Line Scan Intensities for Iron and Titanium Across
Interface of Iron Titanate and AISI-310 Stainless Steel After Testing
for 20,000 Hours at 1350°F

A full section vacuum fusion analysis of the tested specimen after the coating was removed detected 0.044 weight percent of oxygen. This represents almost no change from the as-received material which contained 0.041 weight percent of oxygen.

In summary, the iron-titanate-coated AISI-310 stainless steel tube demonstrated a stable emittance of about 0.88 for 20,000 hours at 1350°F in vacuum. Some changes in the structure of the coating occurred, but they had no observable effect on the emittance of the specimen. Coating separation occurred at the ends of the specimen and in small areas around the black-body holes, but the coating in other areas remained well bonded to the substrate. Only a very limited amount of interaction occurred between the coating and the substrate. Similar to the calcium-titanate-coated tube, substantial amounts of sigma and carbide phases precipitated in the substrate during the test. The lesser as-tested hardness increase observed in this specimen compared to the calcium-titanate-coated specimen is believed to be caused by the slight differences in microstructure commented on above.

3. Iron Titanate on Columbium-1 Percent Zirconium

The columbium-1 percent zirconium tube coated with a 4-mil thick layer of iron titanate completed 10,000 hours of testing in vacuum at 1700°F. At the beginning of the test, the emittance was 0.88, but after 600 hours, it decreased until, at 1800 hours, a value of 0.85 was reached. The emittance remained relatively stable for the remaining period with only a slight decrease from 0.85 to 0.84 during the final 2000 hours. The values for the 10,000-hour test are shown in Figure 49. Throughout the test, a vacuum of 1×10^{-7} torr or better was maintained.

During the test, the specimen was thermally cycled between 1700°F and room temperature 51 times. Thermal cycling produced no adverse effects on the specimen.

The appearance of the specimen at the end of the test at 1700°F and at room temperature is shown in Figure 50. There were no apparent changes in the appearance of the coating other than a slight change in color. No spalling or cracking was evident. A photomicrograph of the coating is shown in Figure 51.

Spectrographic analysis of the coating following testing revealed no significant, changes, as shown in Table XXVIII. X-ray diffraction analysis of the coating revealed the presence of no crystalling phases other than iron titanate.
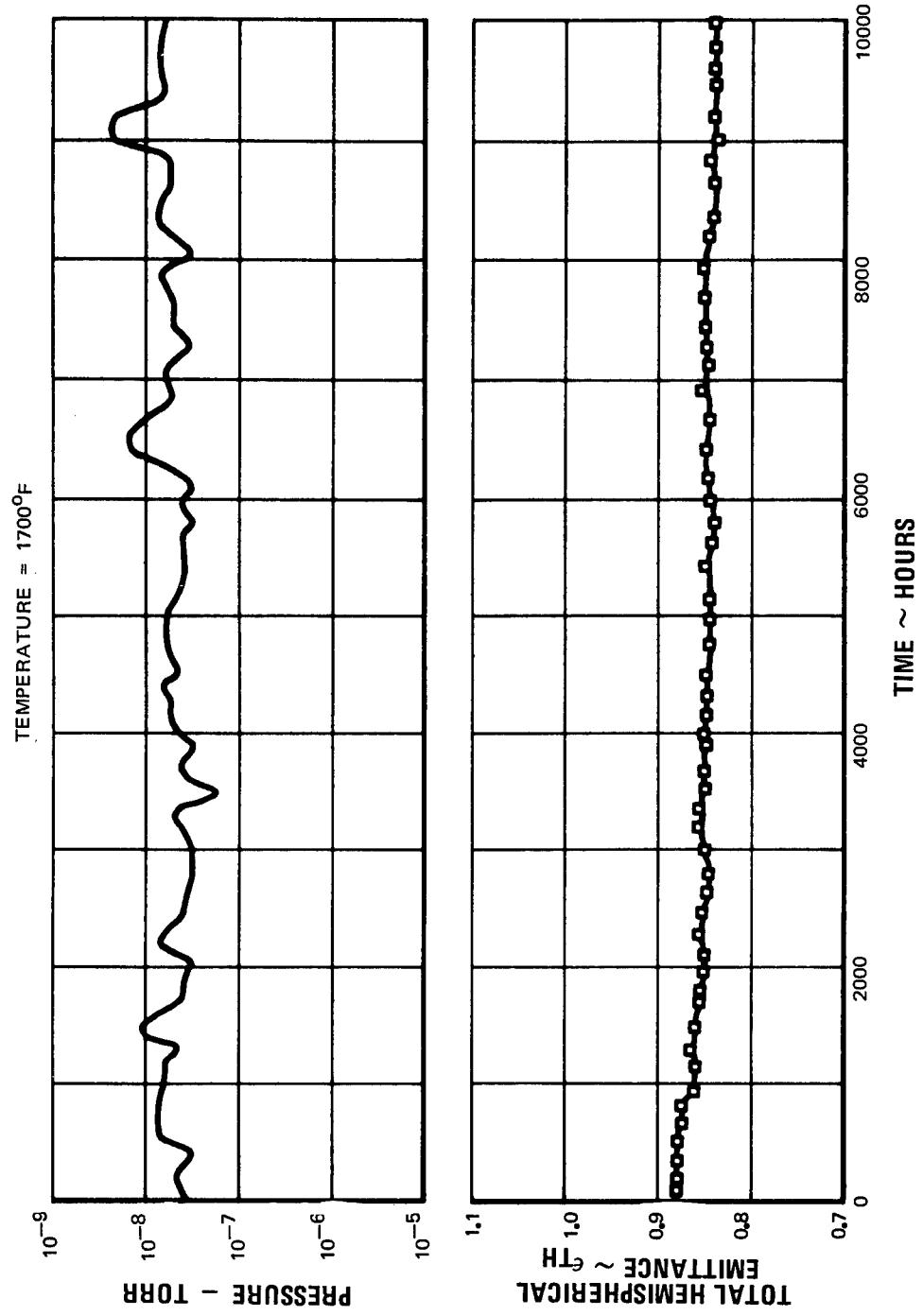
Figure 49   Pressure and Total Hemispherical Emittance for Iron–Titanate–Coated Columbium–1
Percent Zirconium Specimen
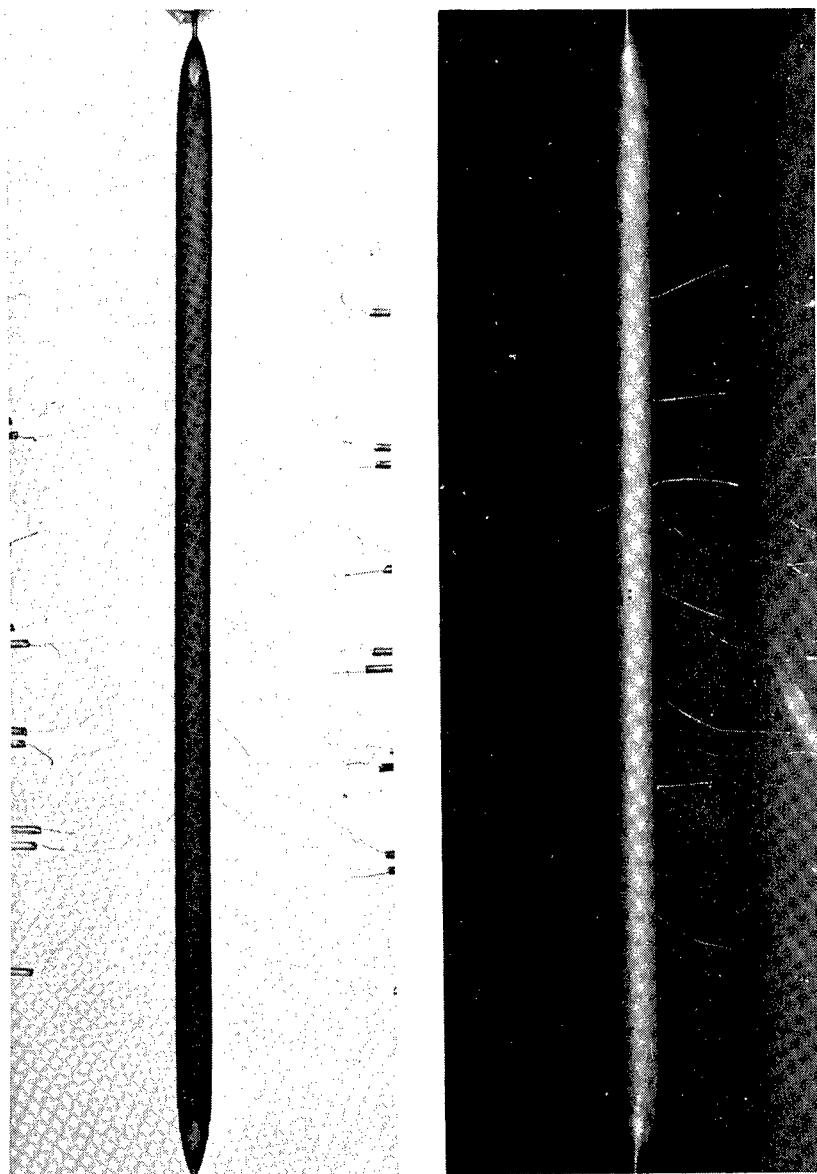
Figure 50   Iron-Titanate-Coated Columbium-1 Percent Zirconium Specimen at
1700°F (Left) and at Room Temperature (Right) After 10,000 Hours
of Testing
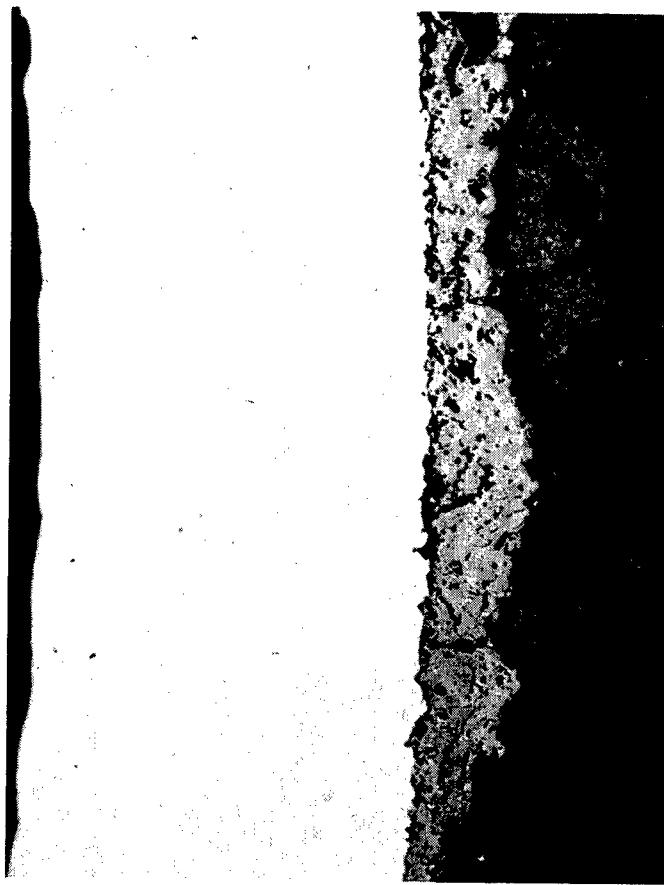
Unetched   Mag: 200X

Figure 51   Photomicrograph of Iron-Titanate on Columbium-1 Percent Zirconium
After 10,000 Hours of Testing at 1700°F

TABLE XXVIII

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF IRON TITANATE ON COLUMBIUM-
1 PERCENT ZIRCONIUM

	Impurity Content (Weight Percent)						
	Mn	Si	Mg	Al	Cr	Ni	Cu
As Received (Powder)	0.5	0.3	0.1	0.7	0.03	–	–
As Sprayed	0.5	0.3	0.1	0.7	0.05	0.02	0.01
10,000 Hours at 1700°F	0.5	0.5	0.2	0.1	–	–	–

The columbium-1 percent zirconium tube was subjected to a detailed analysis before and after testing. Before testing, the tube contained 1.84 weight percent zirconium, 0.01 weight percent carbon, 0.011 weight percent nitrogen, 0.0005 weight percent hydrogen, and 0.032 weight percent oxygen. After testing, vacuum fusion analysis of the entire substrate cross section detected 0.33 weight percent oxygen. In order to determine the distribution of the oxygen, two additional tests were made, one after mechanically removing approximately 3 mils from the outer surface, and the second after mechanically removing about 7 mils, thereby leaving only a 3-mil thickness. The analyses indicated that removing the outer 3 mils lowered the oxygen content to 0.26 weight percent, whereas the 3-mil thickness beneath the inner surface contained 0.32 weight percent. These analyses indicated that the oxygen content increased significantly during the endurance test and that the regions within 3 to 4 mils of each surface contained a higher oxygen content than the center section.

Microhardness traverses were made on cross-section samples of a columbium-1 percent zirconium tube in the as-received condition and on the coated tube after endurance testing. The as-received tube had an average diamond pyramid hardness of 145 kg/mm^2, with essentially no difference in hardness between the surfaces and the center of the cross section. The hardness level measured indicates that the material received on the order of 50 percent cold working following the last heat treatment. A total of six traverses were made across the endurance-tested sample, and, as shown in Figure 52, the hardness was considerably higher close to the surfaces than toward the center of the cross-section, with gradients extending inward about 3 or 4 mils from both surfaces.
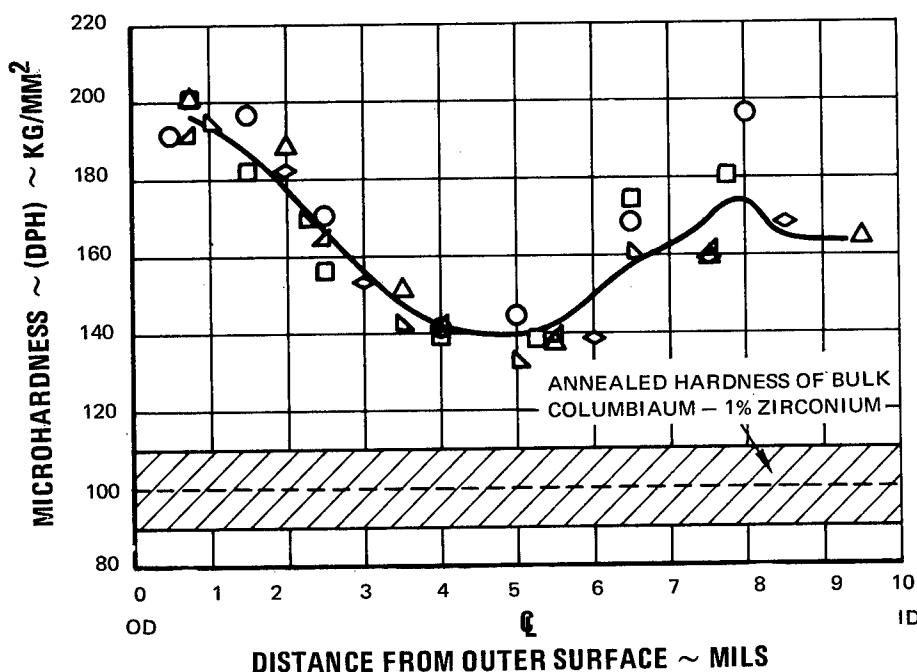
Figure 52   Microhardness Traverse Results for Endurance-Tested Columbium-1 Percent Zirconium Tube Coated With Iron Titanate After 10,000 Hours at 1700°F

The hardness at the center of the cross section is essentially the same as that of the untested tube. The gradients beneath the outer surface were relatively smooth and reproducible, whereas the data for the gradient beneath the inner surface was somewhat erratic. This behavior indicates that diffusion occurred during endurance testing and, possibly, that the diffusion across the outer surface was more uniform than that across the inner surface.

Samples of the columbium-1 percent zirconium material were examined metallographically both before and after endurance testing. The appearance of the substrate after coating and before endurance testing is shown in Figure 53. The microstructure is typical of that for cold-worked columbium-1 percent zirconium. After testing, the microstructure indicates that extensive, but still incomplete, recrystallization occurred (Figure 54). In addition, individual grains are visible on the substrate surface of the coating-substrate interface (see Figure 55). These grains are different in appearance than the remainder of the substrate and may be indicative of the formation of a new phase through interaction of the coating and substrate during testing. (The white regions on both sides of the section are nickel plating applied before polishing to prevent rounding of the specimen edges).
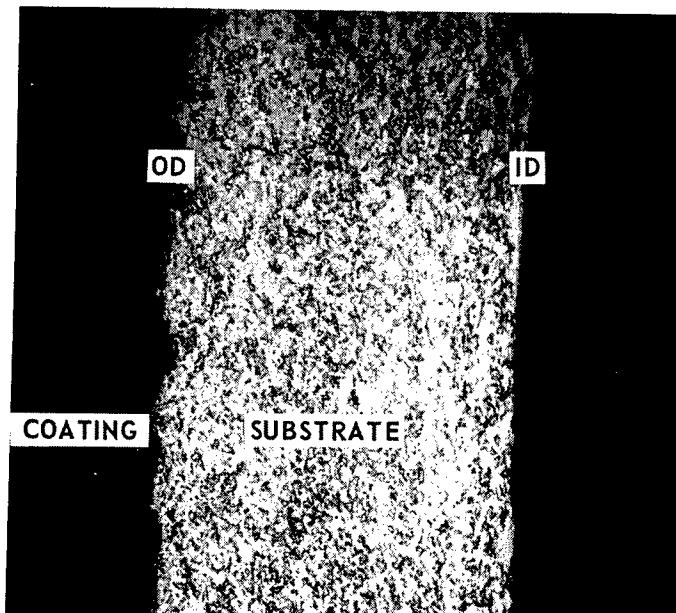
Mag: 200X

Etchant: 10% HF, 30% HNO$_3$, 60% H$_2$O

Figure 53 Cross Sectional Photomicrograph of Columbium-1 Percent Zirconium
Tube After Being Coated With Iron Titanate

82
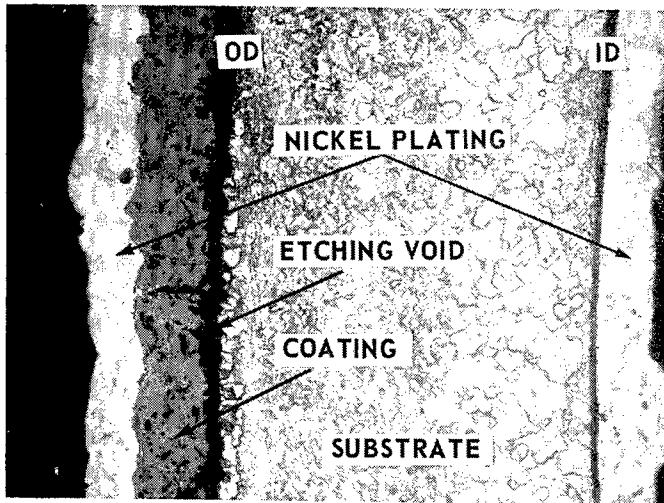
Mag: 200X

Etchant: 10% HF, 30% HNO$_3$, 60% H$_2$O

Figure 54   Cross Sectional Photomicrograph of Iron-Titanate-Coated Columbium-1
Percent Zirconium Tube After Endurance Testing at 1700°F for
10,000 Hours
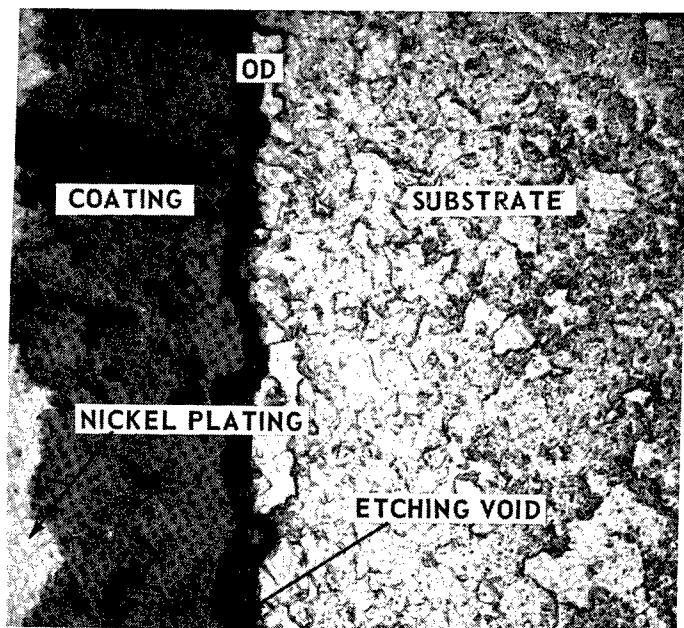
Mag: 500X

Etchant: 10% HF, 30% HNO$_3$, 60% H$_2$O

Figure 55   Cross Sectional Photomicrograph of Iron-Titanate-Coated Colum-
bium-1 Percent Zirconium Tube After Endurance Testing at 1700°F
for 10,000 Hours

Electron-beam microprobe analyses were conducted by the Advanced Metals Research Corporation, Burlington, Massachusetts, on both untested and endurance-tested iron-titanate-coated columbium-1 percent zirconium specimens. The substrate was analyzed for iron and titanium concentations across the entire cross section. An attempt to determine oxygen concentations was also made, but the oxygen level was too low for meaningful data to be obtained. The data for the coated, untested substrate indicated only slight concentrations of iron and titanium. The concentrations at the surface were 0.10 weight percent for both iron and titanium, with the concentrations dropping below the detectability limits at depths of 0.8 mil and 0.7 mil, respectively. This diffusion probably occurred during plasma-arc spraying. The data for the endurance-tested tube (Figure 56) indicates that diffusion of both iron and titanium occurred during testing. The iron content was 0.97 weight percent at the surface and decreased to an undetectable level at a depth of 4 mils. The titanium concentration at the surface was 0.43 weight percent and decreased to an undetectable level within about 1.5 mils.

In addition to the analysis of the substrate, an attempt was made to conduct a microprobe analysis of the coating for the presence of columbium and zirconium. It was not possible to obtain a complete gradient analysis because of the relatively porous nature of the coating. However, point analysis techniques detected the presence of zirconium in isolated regions of the coating. These regions were randomly distributed both radially and circumferentially, and, although not visible optically, the concentrations did fluoresce when excited by the electron beam. No columbium was detected at any point in the coating.

Several observations can be made concerning the data. First, the as-tested microstructure indicates that recrystallization has occurred in some areas of the specimen. From this it can be assumed that recovery is virtually complete in those areas which are not completely recrystallized. In view of the recrystallization that was observed and the long exposure to elevated temperature, it would be expected that the substrate microhardness would be in the range of 90 to 110 kg/mm^2, which is the normal range for cold-worked and annealed columbium-1 percent zirconium.^{2} However, the observed hardness values were at least 40 to 50 kg/mm^2 higher than this, even in the recrystallized regions. This indicates that changes occurred during endurance testing, in addition to recovery and recrystallization, which produced a net increase in material hardness. Two phenomena might account for the increased substrate hardness: metallurgical changes to the precipitates and phases present, and diffusion of material into the substrate. In order to evaluate possible metallurgical changes occurring during testing, it would be necessary to conduct detailed X-ray diffraction and electron microscope analyses. Since this work was not within the scope of the present program, no statement concerning the possibility of such changes can be made. However, diffusion effects can be evaluated on the basis of the microprobe and vacuum fusion oxygen analyses. These analyses indicate that both iron and titanium diffused from the coating into the substrate and that the substrate oxygen content increased during testing.
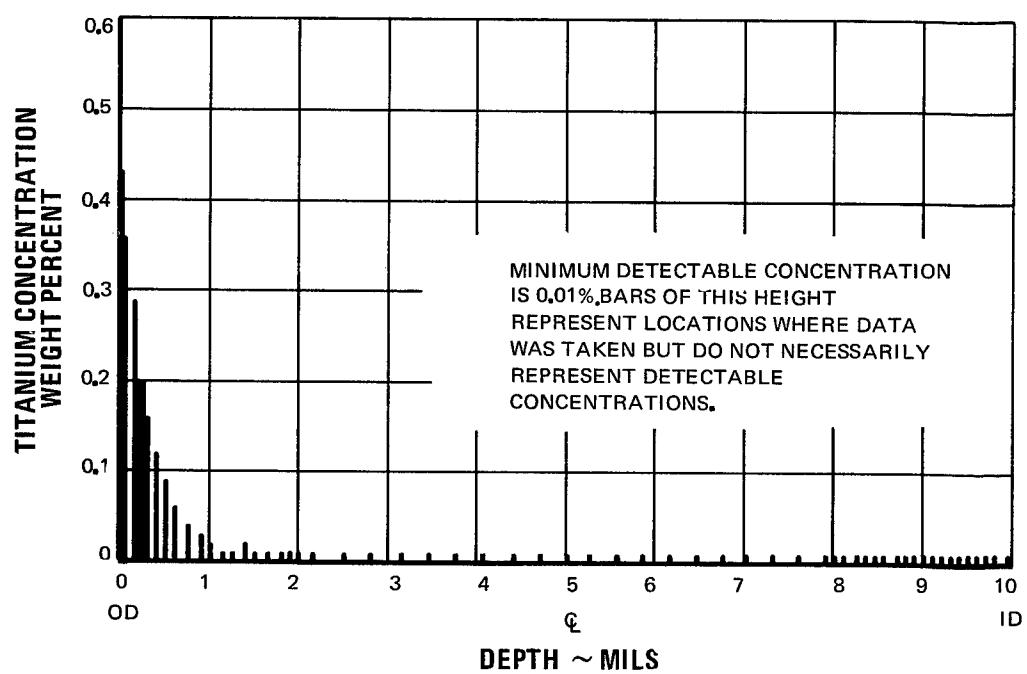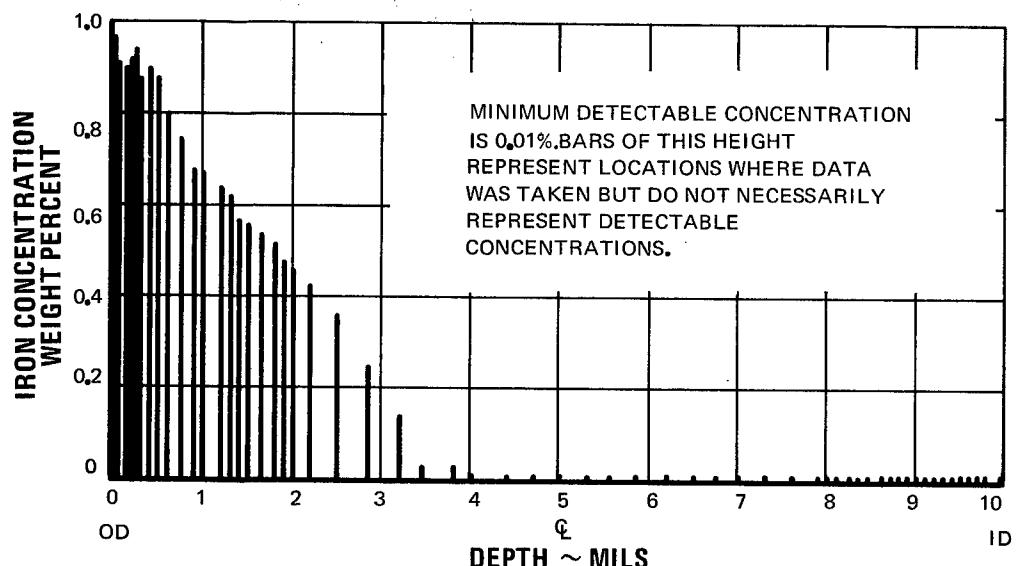
Figure 56   Concentrations of Iron and Titanium Across Columbium-1 Percent Zirconium Tube Coated With Iron-Titanate and Endurance Tested at 1700°F for 10,000 Hours

Investigations of the effects of iron and titanium on columbium alloys indicate that both of these constituents increase the alloy hardness through solid solution strengthening effects. Specifically, 1 weight percent of iron has been found[3] to increase the diamond pyramid hardness by 50 kg/mm^2 over the base hardness, and 1 weight percent of titanium increased the hardness by 40 kg/mm^2. On the basis of the known concentrations of iron and titanium in the substrate, the corresponding increases in hardness were calculated for each mil of depth into the substrate for which detectable concentrations of these elements were found. Subtracting the values calculated from the average measured substrate hardness results in the lower curve shown in Figure 57. As shown, virtually all of the hardness gradient detected at the outer surface of the substrate can be accounted for by the solid solution hardening effects of the iron and titanium in this region.
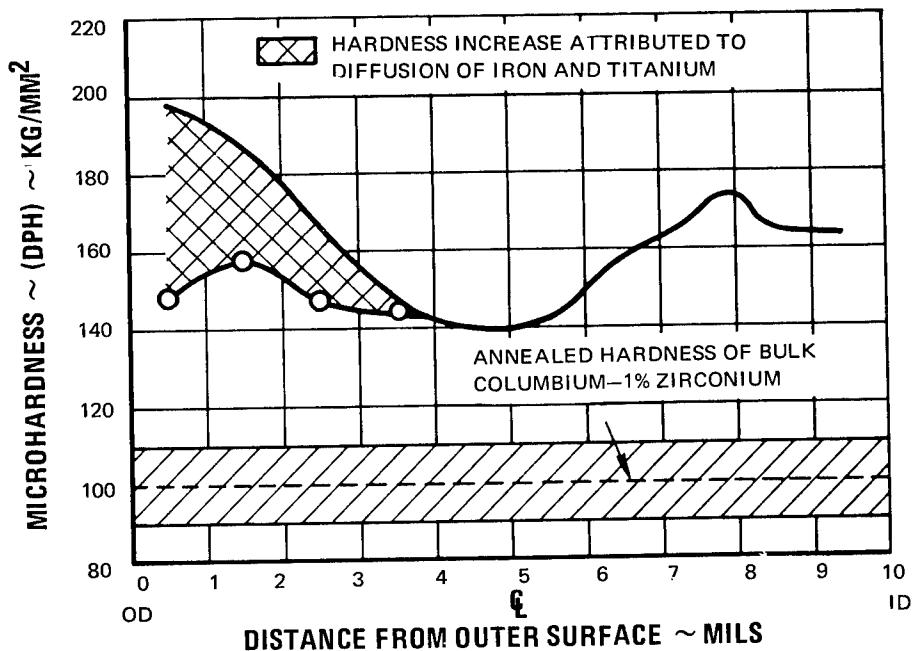
Figure 57   Effect of Iron and Titanium Diffusion on Hardness of Columbium-1 Percent Zirconium Tube Coated With Iron Titanate and Endurance Tested at 1700°F for 10,000 Hours

The hardness gradient found on the inner surface as well as the general elevation of hardness across the entire cross section above that anticipated remains to be explained. The possible hardening effects of the increased oxygen content were considered. Investigators have reported[3] that an increase of 0.1 weight percent of oxygen in columbium produces an increase in hardness of 85 kg/mm^2.

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This hardness is caused by a solid solution strengthening effect. In the case of oxygen diffusion into columbium-1 percent zirconium, it would be expected that, because of the high activity of zirconium, the initial quantities of oxygen entering the alloy would preferentially combine with the zirconium and precipitate as zirconium-oxide particles. This precipitate would have little, if any, effect on the room temperature hardness of the alloy. This mechanism for the effective removal of both zirconium and oxygen from the alloy would continue until all of the available zirconium had been used up.

Once that point is reached, however, any additional oxygen entering the alloy would dissolve in the columbium matrix and produce a solution hardening effect. This mechanism can be applied to the substrate under investigation, which has been found to contain 0.72 percent zirconium. On a stoichiometric basis, this quantity of zirconium would react with 0.25 percent oxygen. Hence, the first 0.25 percent oxygen diffusing into the substrate, while physically present, would not be available for solution hardening of the columbium. The quantity of oxygen required to produce the observed general hardness level increase of 40 to 50 kg/mm^2 can be calculated and is found to be 0.05 weight percent. Adding this to the oxygen calculated to combine with zirconium (0.25 percent) yields a value of 0.30 percent as the calculated oxygen content for the entire substrate cross section. This value compares well with the overall specimen oxygen content of 0.33 percent determined by vacuum fusion analysis.

Oxygen diffusion also appears to be responsible for the hardness gradient observed beneath the inner surface. The total solid-solution oxygen required to produce the peak hardness shown at the inner surface would be approximately 0.09 percent. Adding this to the 0.25 percent oxygen which combines with zirconium yields 0.34 percent oxygen at the inner surface. This value is consistent with the results of the partial section vacuum fusion analysis which indicated an oxygen gradient in this area.

It should be emphasized at this point that the mechanisms postulated above to explain the microstructural hardness and compositional results obtained on the tested substrate have not been verified. Considerably more refined and detailed testing and analysis would be necessary. As stated previously, it is entirely possible that changes in the composition and structure of the metallurgical phases present in the substrate, which it has not been possible to examine, play a part in producing the observed results. It is felt, however, that the postulated mechanism does explain all of the observed phenomena in general terms and that it provides a starting point for further investigations.

There are several possible sources of the oxygen which diffused into the substrate. The existence of an oxygen gradient extending inward from both substrate surfaces indicates that oxygen diffusion occurred across both surfaces.

The obvious source of oxygen for the outer surface is the iron-titanate coating. The fact that diffusion across the coating-substrate interface occurs has already been demonstrated by the presence of iron and titanium in the substrate. For the inner surface, there are two possible sources of oxygen. First, it is possible that a thin oxide layer was formed on the inner surface during plasma-arc spraying of the coating. During the endurance test, the oxygen in the oxide layer might be expected to diffuse into the substrate. The second source is the residual gases in the test chamber. It has been found that columbium absorbs significant quantities of oxygen from the residual gases in a vacuum. For example, H. Inouye[4] found an increase in oxygen content of approximately 125 ppm in columbium specimens exposed to a vacuum of 1×10^{-7} torr for 1000 hours at 1700°F. It would be expected that exposure to these conditions for the longer periods for this program would result in even higher oxygen levels. From this, it would appear that the hardness gradient observed on the inner surface is attributable to oxygen contamination resulting from the specimen coating techniques used as well as the specific test environment and is not the result of a coating-substrate interaction.

In summary, post-test analysis of the iron-titanate-coated columbium-1 percent zirconium tube revealed that iron and oxygen, and to a lesser extent, titanium, diffused into the substrate during the 10,000-hour exposure to vacuum and a temperature of 1700°F. Microhardness gradients extending inward from both substrate surfaces were found, as was a general increase in overall hardness compared to that expected on the basis of the microstructure. A tentative explanation for the observed hardness changes has been postulated on the basis of the diffusion detected. However, in spite of the various phenomena which occurred during the tests, neither a serious loss in the emittance of the coating nor any degradation of the coating integrity or adherence was observed.

4. Aluminum Oxide Aluminum Titanate on Columbium-1 Percent Zirconium

The columbium-1 percent zirconium tube coated with a 4-mil thick layer of aluminum oxide aluminum titanate was tested for 10,000 hours at 1700°F in vacuum. The specimen was thermally cycled 63 times between the test temperature and room temperature during the test with no visible adverse effects on the specimen. The appearance of the specimen at 1700°F shortly before the end of the test is shown in Figure 58.

Initially, the specimen had an emittance of 0.87, but the emittance dropped steadily throughout the test, reaching a value of 0.80 at the completion of the test. A vacuum of 1×10^{-7} torr or better was maintained throughout the test. These data are shown in Figure 59.
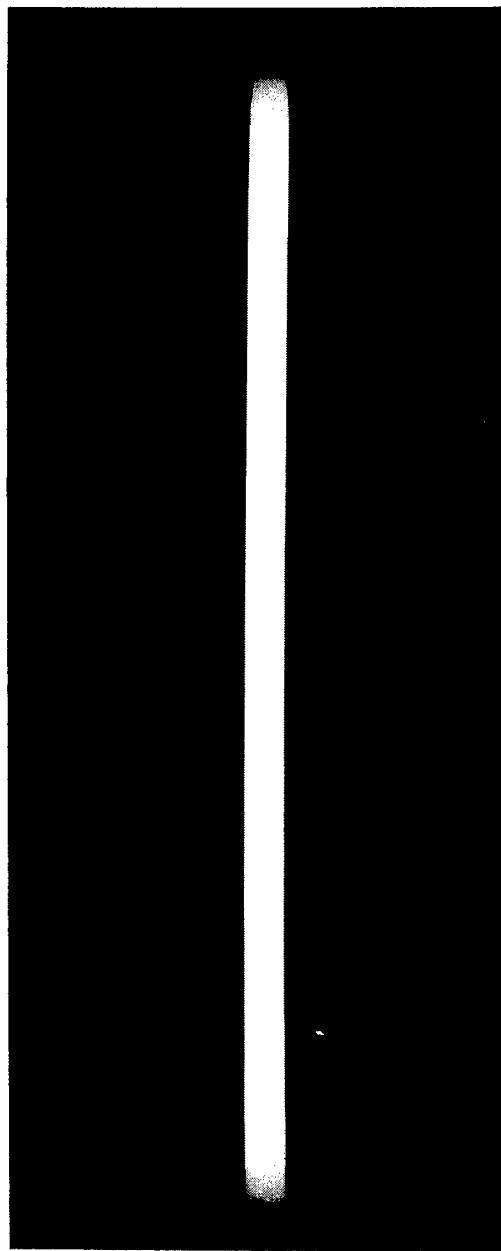
Mag: 0.9X

Figure 58 Aluminum-Oxide-Aluminum-Titanate-Coated Columbium-1 Percent
Zirconium Tube at 1700°F in Vacuum Prior to Completion of 10,000
Hours of Testing

X-21860

TEMPERATURE: 1700°F
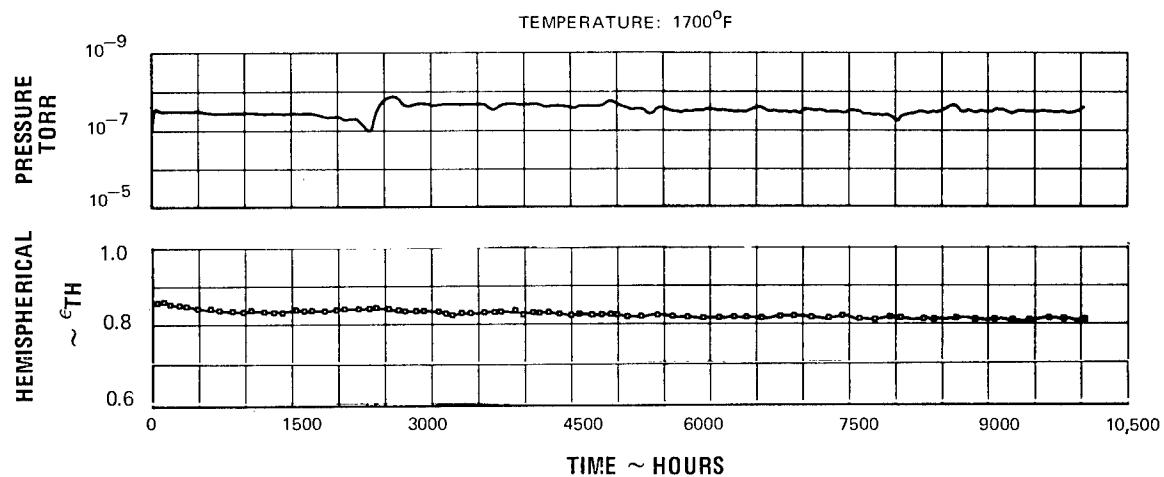
Figure 59 Pressure and Total Hemispherical Emittance for Long-Term En-
durance Test of Aluminum-Oxide-Aluminum-Titanate-Coated
Columbium-1 Percent Zirconium

The appearance of the coating after testing is shown in Figure 60, together with
a coated, untested specimen. It is evident that substantial changes occurred.
No spalling or cracking of the coating occurred, but the color changed from a
uniform light gray to a much whiter color mottled with gray patches. This
change was first observed after approximately 9000 hours of testing.
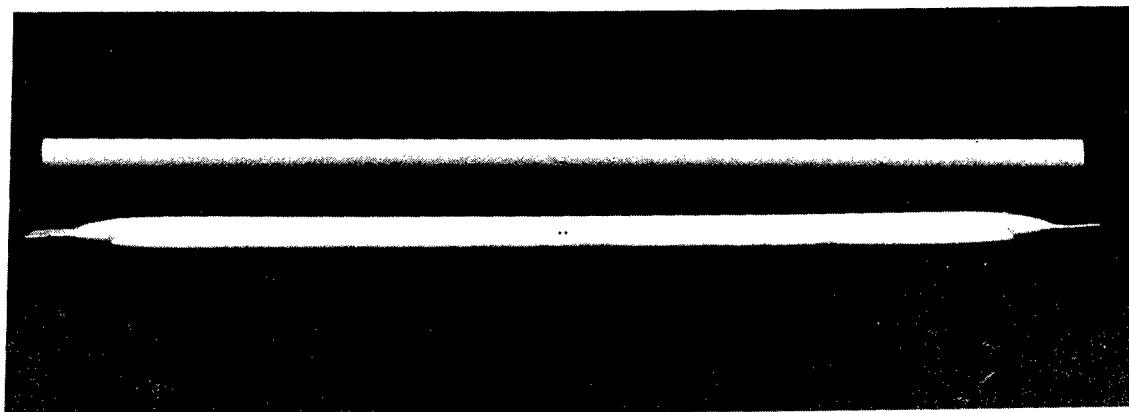
Mag: 0.5X

Figure 60 Appearance of Aluminum-Oxide-Aluminum-Titanate-Coated Colum-
bium-1 Percent Zirconium Tube Before (Top) and After (Bottom)
Testing for 10,000 Hours at 1700°F   XP-64742

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After testing, the specimen was sectioned for metallographic examination. The specimen cross section is shown in Figure 61. The substrate microstructure prior to testing was the same as that for the iron-titanate-coated columbium-1 percent zirconium tube shown in Figure 53. Photomicrographs of the coating-substrate interface are shown in Figures 62 and 63. The specimen shown in Figure 63 was etched to show the formation of a second phase at the coating-substrate interface. The layer was less than 0.1 mil thick and was virtually continuous around the interface circumference.
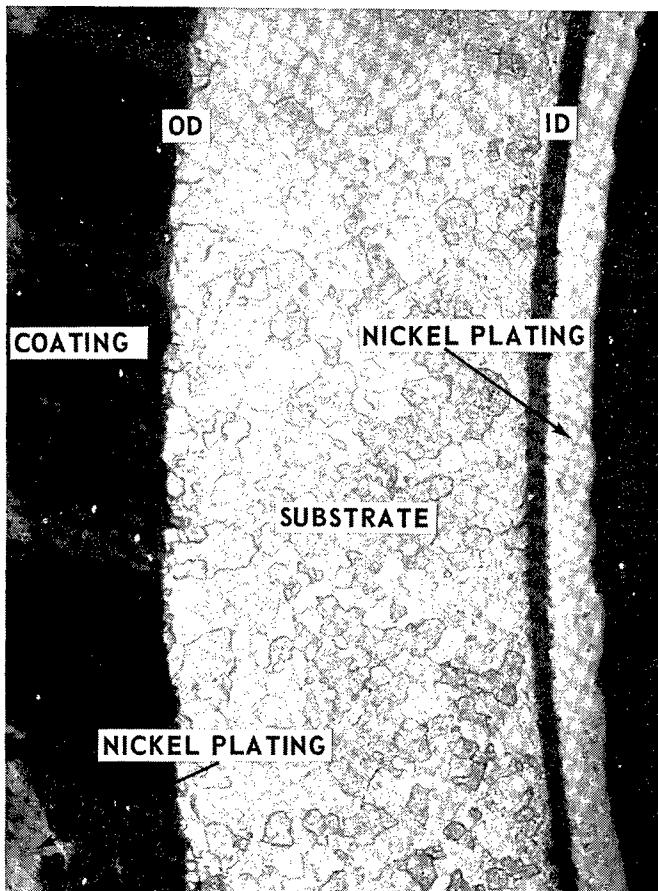
Mag: 200X

Etchant: 10% HF, 30% HNO3, 60% H2O

Figure 61 Cross Sectional Photomicrograph of Aluminum-Oxide-Aluminum-Titanate-Coated Columbium-1 Percent Zirconium Tube After Endurance Testing at 1700°F for 10,000 Hours
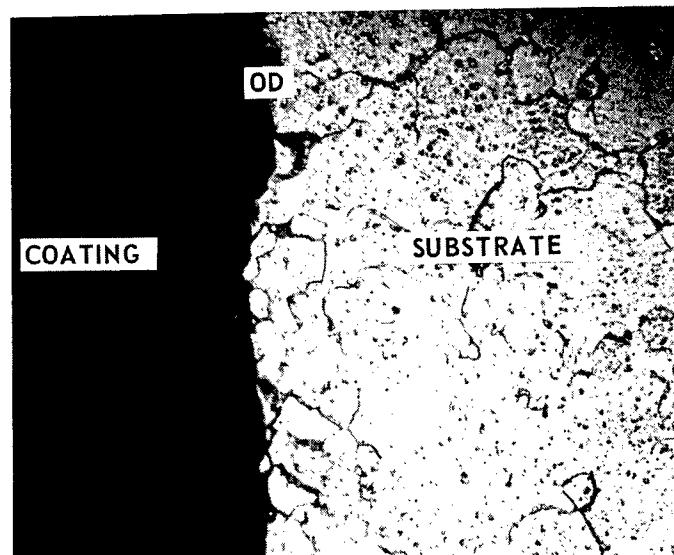
Mag: 500X

Etchant: 10% HF, 30% HNO$_3$, 60% H$_2$O

Figure 62   Cross Sectional Photomicrograph of Aluminum-Oxide-Aluminum-
Titanate-Coated Columbium-1 Percent Zirconium Tube After En-
durance Testing at 1700°F for 10,000 Hours
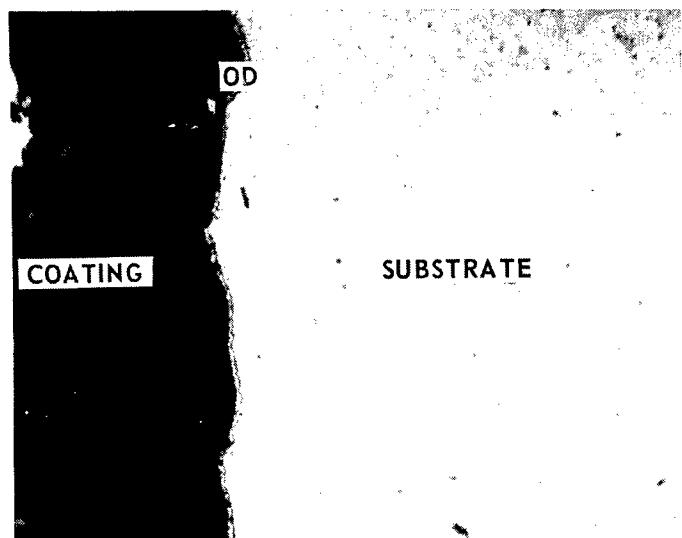
Etchant: 10% HF, 90% H$_2$O   Mag: 500X

Figure 63   Cross Sectional Photomicrograph of Aluminum-Oxide-Aluminum-
Titanate Coated Columbium-1 Percent Zirconium Tube After Endu-
rance Testing for 10,000 Hours at 1700°F (Photomicrograph has been
etched to show second phase at coating-substrate interface).

A total of four microhardness traverses were made on the substrate cross
section, and the results are presented in Figure 64. The results indicate a
slight increase in hardness in the interior of the substrate, but the variation is
within the accuracy limits of the test technique and probably does not represent
a true increase. The overall hardness is equal to that expected for fully recrystal-
lized columbium-1 percent zirconium. The hardness of the phase at the coating-
substrate interface could not be measured because of its thinness.
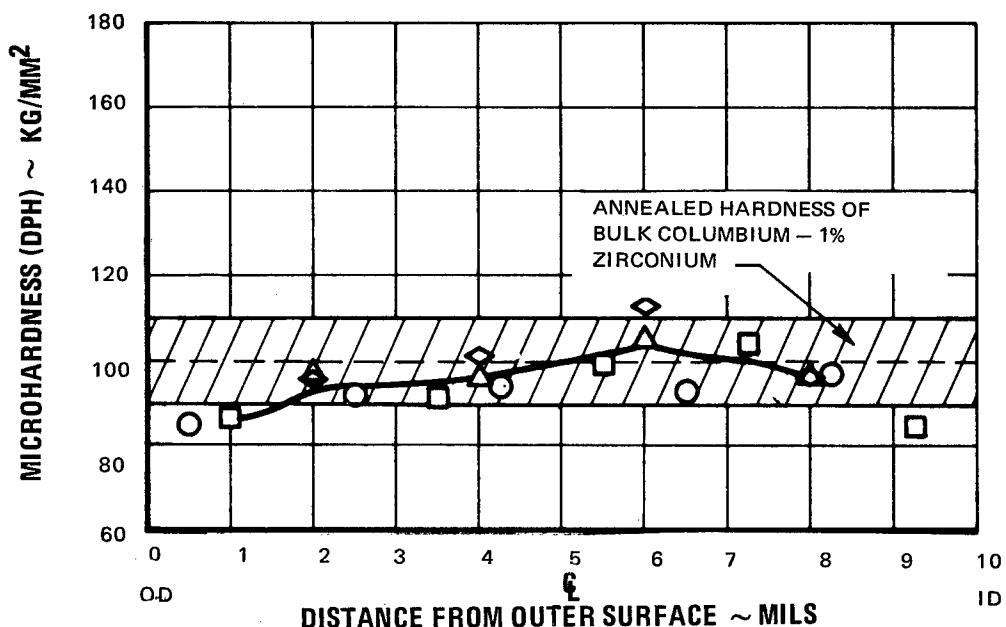
Figure 64   Microhardness Traverse Results for Columbium-1 Percent Zirconium
            Tube Coated With Aluminum Oxide Aluminum Titanate and Endurance
            Tested for 10,000 Hours at 1700°F

Electron-beam microprobe analyses were conducted for aluminum and titanium
concentrations in the tested substrate. The results are presented in 65. As
shown, high, steep gradients were detected for aluminum and titanium at the
coating-substrate interface, indicating that the interface phase shown in Figure 63
is a quarternary alloy of aluminum, titanium, zirconium, and columbium. The
results also show a very shallow aluminum gradient extending through virtually
the entire section.
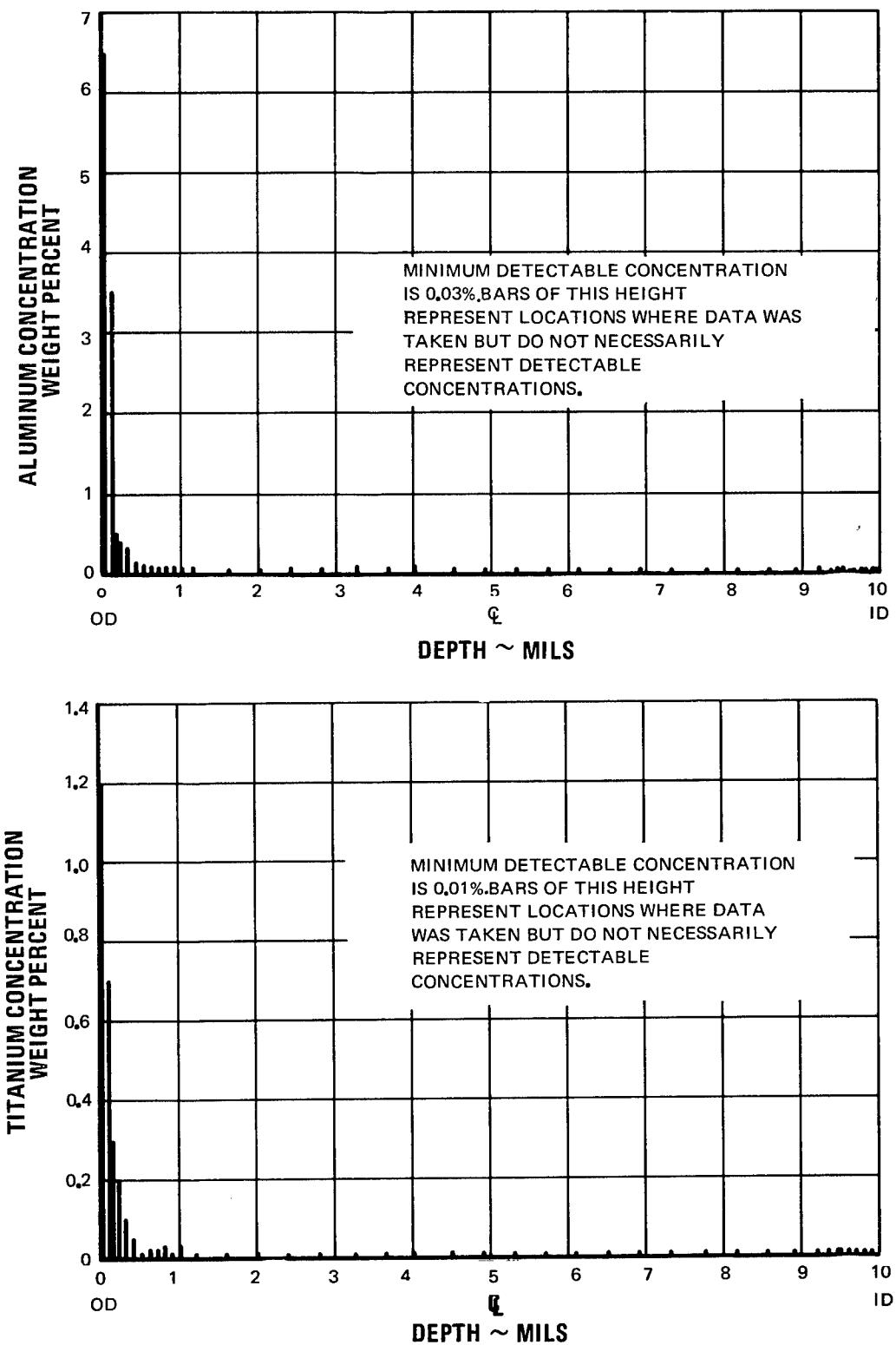
Figure 65   Concentrations of Aluminum and Titanium Across Columbium-1
Percent Zirconium Tube Coated With Aluminum-Oxide-Aluminum
Titanate and Endurance Tested at 1700°F for 10,000 Hours

A vacuum fusion analysis for oxygen content was conducted on the full section of the substrate after the coating was removed mechanically and by acid etching. An oxygen content of 0.145 percent was found. The fact that this specimen had so high an oxygen content but still had a hardness equal to that associated with columbium-1 percent zirconium alloys with lower oxygen concentrations provides substantiation for the assumption made for the iron-titanate-coated specimen that oxygen is ineffective as a solid solution hardening agent until it has reacted with all of the available zirconium.

A spectrographic analysis was made on the coating material both before and after testing, and the results are shown in Table XXIX.

TABLE XXIX

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF ALUMINUM OXIDE-ALUMINUM
TITANATE APPLIED TO BERYLLIUM

	Impurity Content (Weight Percent)				
	Cu	Fe	Mg	Mn	Si
As Received (Powder)	<0.01	0.5	0.6	trace	0.1
As Sprayed	<0.01	0.05	0.4	trace	0.1
After Endurance Test	<0.01	<0.01	0.01	0	<0.01

Note: Powder obtained from the Zirconium Corporation of America.

Detailed visual examination of the coating showed that the portions of the coating which appeared white consisted of three layers: a white layer on the outer surface, a light gray layer very similar to the as-sprayed coating, and, at the substrate surface, a thin, dense, very dark gray layer. In those portions of the coating which showed the darker, mottled appearance, the white layer was either very thin or nonexistent.

In order to understand the reactions which had occurred, X-ray diffraction analyses were conducted on the various portions of the coating. The results are presented in Table XXX. As shown, only a questionable indication of the presence of aluminum titanate was found after testing. This indicates a virtually complete breakdown of the titanate compound. Some columbium diffusion evidently occurred during testing. The gray areas would appear to contain significant quantities of columbium both as a columbium-aluminum intermetallic compound and possibly as columbium oxide. The white areas, however, were found to be free of these compounds and consisted almost completely of aluminum and titanium oxides. From these results, it is concluded that the reactions in the coating were initiated at the coating-substrate interface and moved slowly outward. This behavior appears to explain why no change in the coating was observed until after some 9,000 hours of testing.

TABLE XXX

X-RAY DIFFRACTION ANALYSIS RESULTS FOR ALUMINUM OXIDE-
ALUMINUM TITANATE COATING APPLIED TO COLUMBIUM-1
PERCENT ZIRCONIUM TUBE AND ENDURANCE TESTED
AT 1700°F FOR 10,000 HOURS

As Received (Powder) Al_2O_3, TiO_2, Al_2TiO_5, possibly TiO

After Testing (Coating)
    Full Cross Section Al_2O_3, TiO_2, Ti_2O_3, $CbAl_3$, CbO_2
    White Area Al_2O_3, TiO_2, possibly Al_2TiO_5
    Gray Area Al_2O_3, $CbAl_3$, probably TiO and CbO_2

Note: Powder obtained from the Zirconium Corporation of America.

In summary, endurance testing and analysis of an aluminum oxide aluminum
titanate coating on columbium-1 percent zirconium indicated that the coating
remains well bonded to the substrate for 10,000 hours at a temperature of
1700°F but that the coating is not sufficiently stable to maintain its chemical
composition and emittance properties in the test environment. This would
indicate that aluminum oxide aluminum titanate is not a suitable coating material
for space radiator applications at 1700°F.

IV. THERMAL CYCLING TESTS

A. INTRODUCTION

Two columbium-1 percent zirconium tubes coated with iron titanate were sub-
jected to thermal cycling in vacuums of 1×10^{-7} torr or better. One specimen
was cycled between 1500°F and 1800°F for 5,000 hours, and the other was cycled
between 1500°F and 1900°F for 10,000 hours to simulate a potential solar receiv-
er temperature cycle. The thermal cycling sequence used is shown in Figure
66. Both specimens were subjected to thorough chemical and metallurgical
analyses following testing.

The iron titanate used for these specimens was obtained from the Continental
Coatings Corporation and was designated FCT-11, special process, special size.
According to the supplier, this material was produced by sintering fines of
FCT-11 material and subsequently grinding it to a size suitable for plasma spraying.
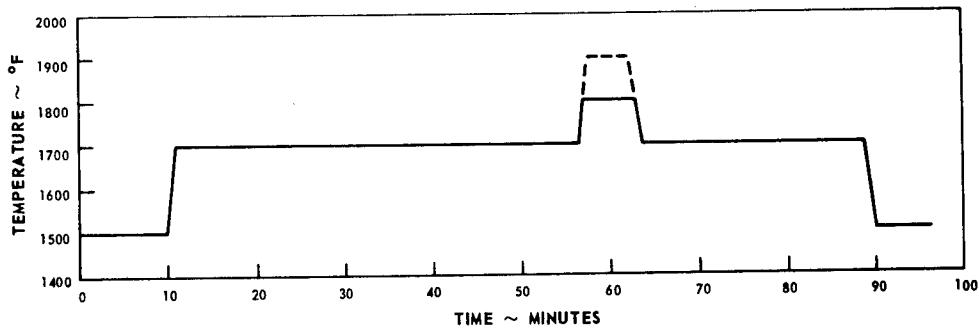
Figure 66   Thermal Cycling Sequence Used in 1500°F to 1800°F and 1500°F to
           1900°F Cycling Endurance Tests

B. THERMAL CYCLING EQUIPMENT

The equipment used for two of the long-term endurance tests was modified for
the thermal cycling tests. The modifications entailed replacement of the ion
pump elements to provide greater reliability, and design, construction, and
installation of an electromechanical device to automatically thermal cycle the
specimens. The device consisted of a multiswitch timer, a 250-rpm DC motor,
and a number of microswitches. The motor drove the powerstat through a
speed-reducing gear train. The direction of rotation and the starting time for
changing the powerstat setting was controlled by the timer. The drive motor
was stopped at the powerstat control positions corresponding to the desired
specimen temperatures by microswitches mounted on the back of the powerstat.
Safety microswitches were also provided to prevent the powerstat control from
being rotated either above the maxiumum temperatures or below the minimum
temperature in the event that one of the other switches failed. Opening the
microswitch at the upper limit deactivated the circuit for increasing the power-
stat setting, but still permitted the setting to be reduced by the timer circuit.

Opening the microswitch at the lower limit deactivated the entire control circuit. Consequently, failure of any of the control microswitches would result in the specimen temperature being reduced to and maintained at 1500°F. The cycling operation was continously monitored by recording the specimen heating current on a strip chart recorder.

C. SPECIMEN PREPARATION

The specimens used for the thermal cycling tests were columbium-1 percent zirconium tubes coated with iron titanate. The tubes were 9 inches long, 0.250 inch in diameter, and had a 0.010-inch wall thickness. They were identical to those used for long-term endurance testing. Analysis indicated that the tubes contained 1.84 weight percent zirconium, 0.01 weight percent carbon, 0.011 weight percent nitrogen, 0.0005 weight percent hydrogen, and 0.032 weight percent oxygen. The tubes were prepared for coating by grit blasting with 60-mesh silicon at 80 psi to a roughness height of about 100 microinches AA (arithmetic average).

The iron-titanate powder used was obtained from the Continental Coatings Corporation and was designated FCT-11, special process, special size. The powder was somewhat coarser than that used earlier in the program. Use of the coarser powder eliminated compaction in the spray gun hopper. Semi-quantitative spectrographic analysis of the powder detected the presence of 0.5 percent aluminum, 0.2 percent magnesium, 0.4 percent manganese, 0.2 percent chromium, 0.4 percent silicon, and a trace of copper. X-ray diffraction analysis indicated that iron titanate was the only crystalline phase present.

Coatings which were approximately 4 mils thick were applied by plasma-arc spraying, using argon as both the arc gas and the powder carrier gas. The plasma-spray parameters used are shown in Appendix A. After spraying, scrapings of the coatings were analyzed. Spectrographic analysis revealed approximately the same concentrations of impurities as found previously, and X-ray diffraction analysis indicated that iron titanate was still the only crystalline phase present. One of the coated specimens is shown in Figure 67.

D. TEST AND ANALYSIS RESULTS

1. Specimen Cycled Between 1500°F and 1800°F

The specimen cycled between 1500°F and 1800°F was tested for a total of 5000 hours and was cycled 3,125 times. Of the total 5000 hours of testing, 820 hours were at 1500°F, 3835 hours were at 1700°F, and 255 hours were at 1800°F. The remaining 90 hours were used for heating and cooling the specimen.
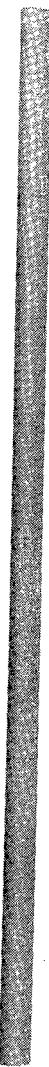
Mag: 0.5X

Figure 67   Appearance of Iron-Titanate-Coated Columbium-1 Percent Zirconium
          Thermal Cycling Specimen Before Testing   XP-71059

Thermal cycling appeared to have no adverse effects on the specimen, although
a small wedge-shaped hair-line crack appeared after about 3500 hours of test-
ing. This crack was evident when the specimen was heated, as shown in
Figure 68, but was extremely difficult to see after testing when the specimen
was cooled to room temperature. The crack is not visible in the photograph
of the specimen after testing (Figure 69). As shown, aside from the crack, no
visible changes occurred as a result of testing. The texture and color of the
coating were the same as before testing, and there was no indication of coating
separation or spalling.
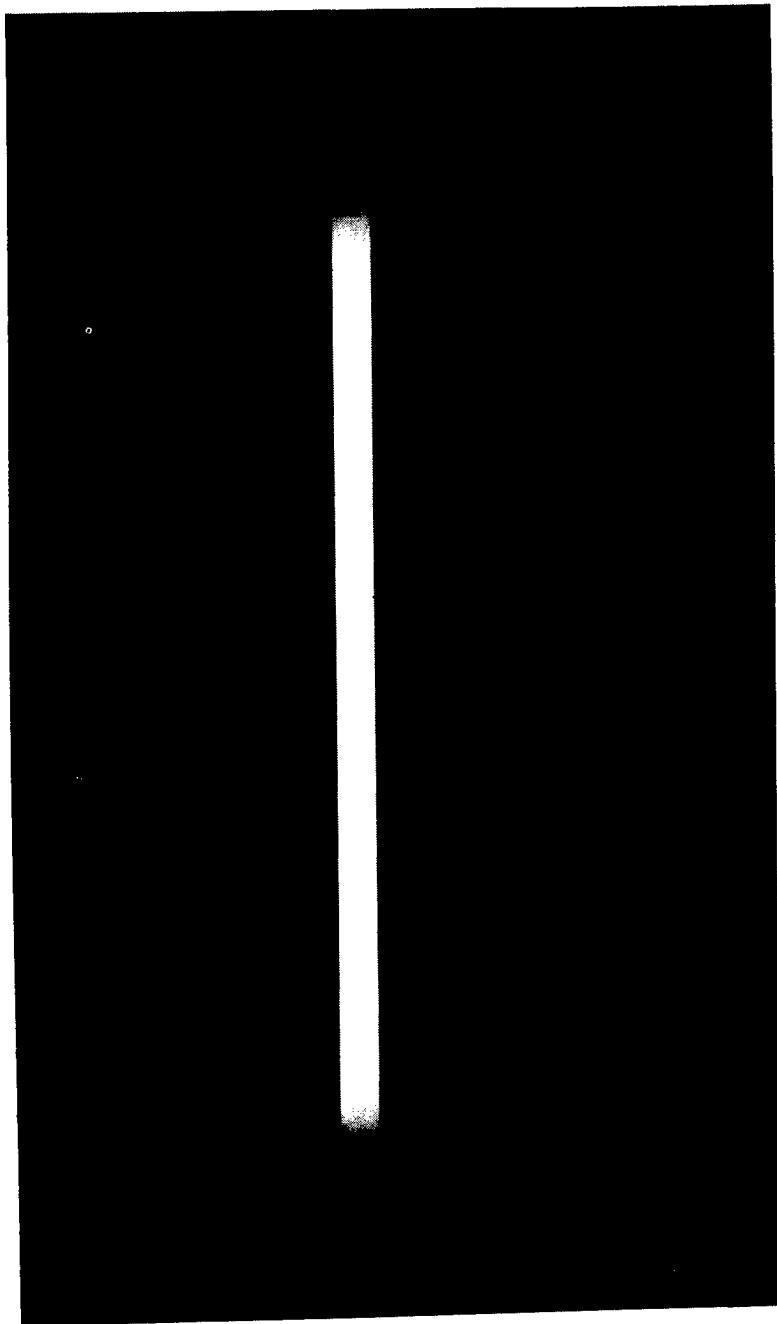
Mag: 0.7X

Figure 68   Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube at
1700°F in Vacuum Prior to Completion of 5,000-Hour 1500° to
1800°F Cycling Test

X-24554
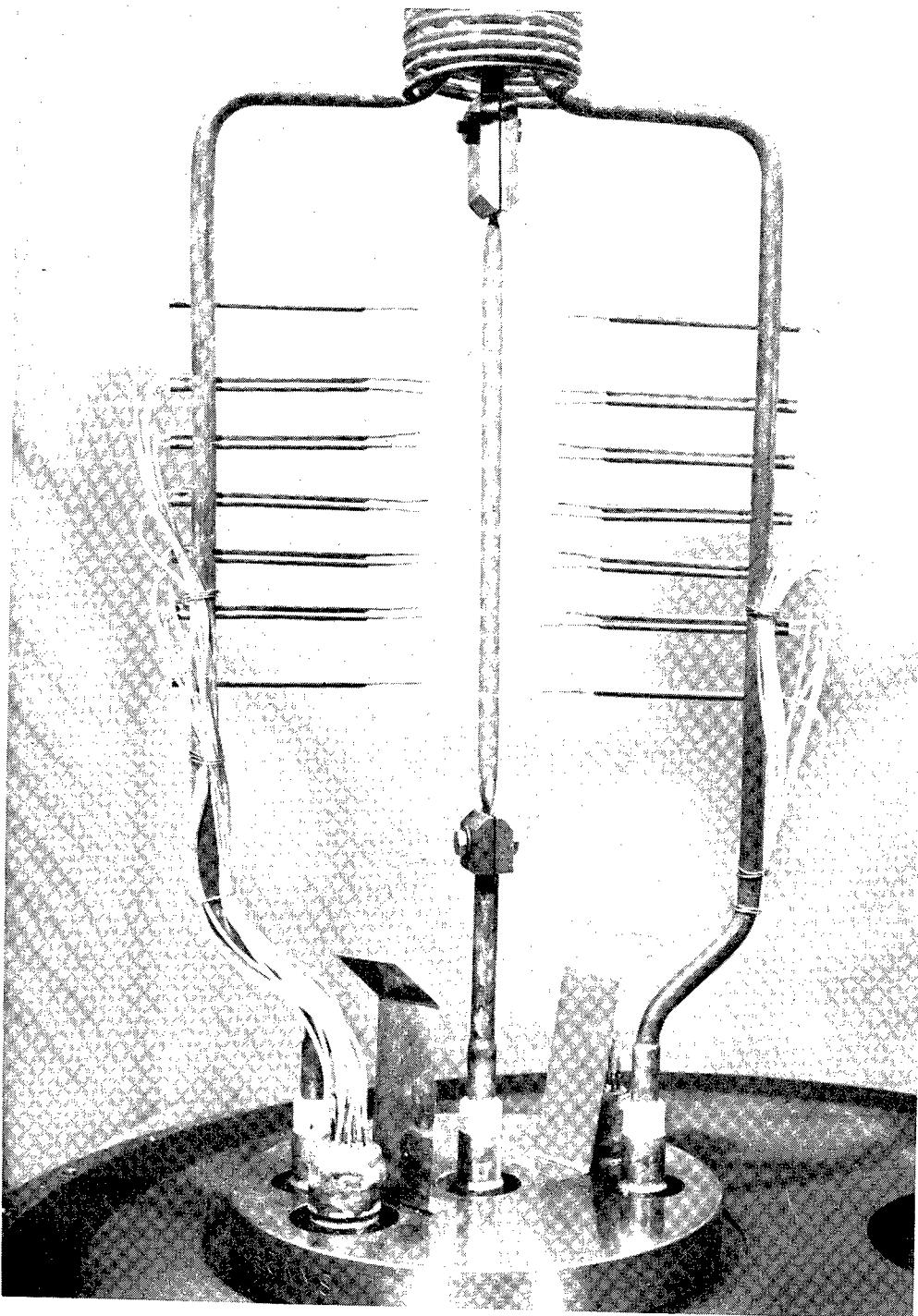
Figure 69   Appearance of Iron-Titanate-Coated Columbium-1 Percent Zir-
conium Tube Thermally Cycled for 5, 000 Hours Between 1500° and
1800°F

X-24557

The emittance and vacuum measured during the test are shown in Figure 70. As shown, the emittance was stable at about 0.88 at 1800°F throughout the test, and a vacuum of 1×10^{-7} torr or better was maintained in the test chamber.
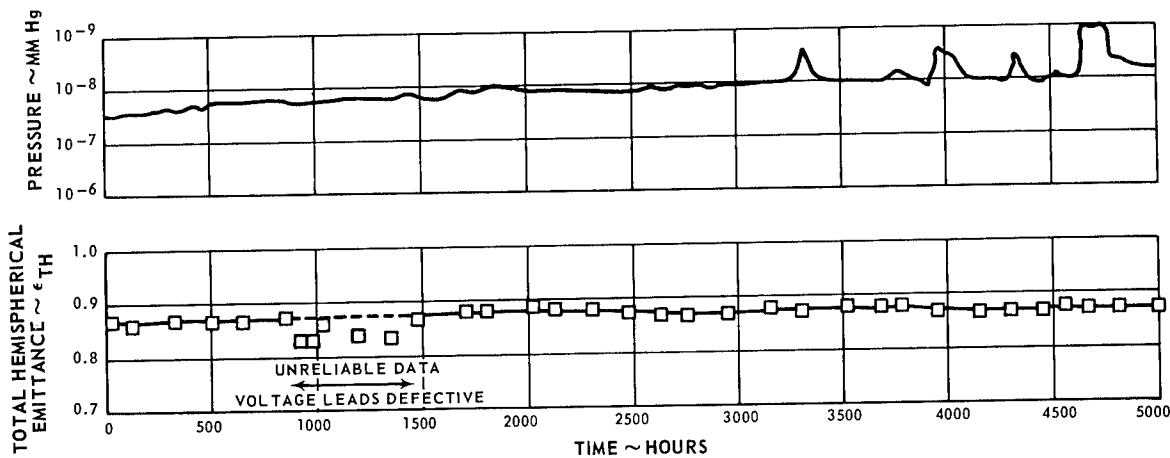
Figure 70   Pressure and Total Hemispherical Emittance for Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube Cycled Between 1500 and 1800°F

After testing, the coating was analyzed by spectrographic and X-ray diffraction analyses. The results of the spectrographic analysis are shown in Table XXXI. Only small changes in the impurities present occurred during testing. The X-ray diffraction analysis showed that some changes in the structure of the coating occurred. Before testing, the coating was entirely iron titanate, but after testing, the phases present were iron titanate and titanium oxide. The relative intensities of the major diffraction lines for these materials indicated that they were present in about equal amounts.

TABLE XXXI

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS
OF IRON TITANATE ON COLUMBIUM-1
PERCENT ZIRCONIUM

| | Impurity Content (Weight Percent) | | | | | |
	Al	Mg	Mn	Cr	Si	Cu
As Sprayed	0.5	0.2	0.4	0.2	0.4	trace
After Test	0.5	0.5	1.0	0.1	0.5	trace

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The columbium-1 percent zirconium substrate was examined metallographically, and the results are shown in Figures 71 and 72. The specimen shown in Figure 71 was etched to reveal the substrate grain structure, and the specimen shown in Figure 72 was unetched to show that no coating separation occurred. The appearance of the substrate microstructure indicates that partial recrystallization occurred during testing.
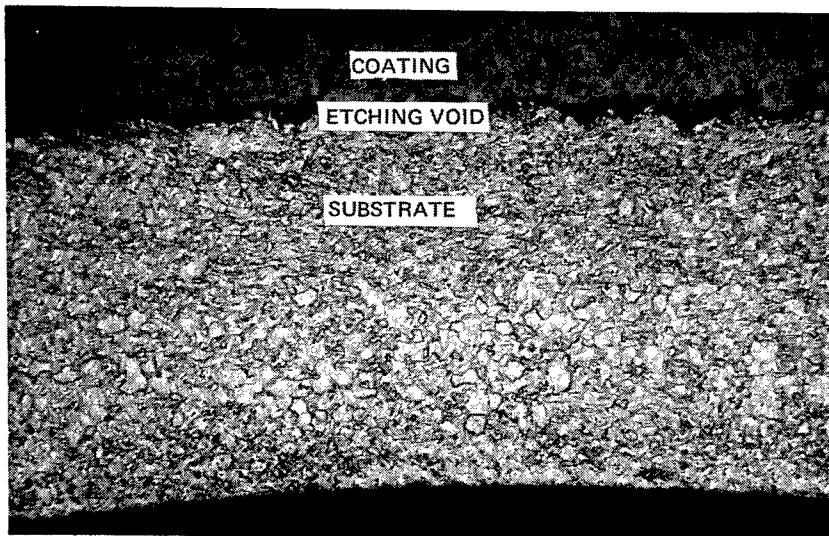
Etchant: 10% HF, 30% HNO$_3$, 60% H$_2$O   Mag: 200X

Figure 71   Photomicrograph of Columbium-1 Percent Zirconium Tube Coated With Iron Titanate and Cycled Between 1500 and 1800°F for 5,000 Hours
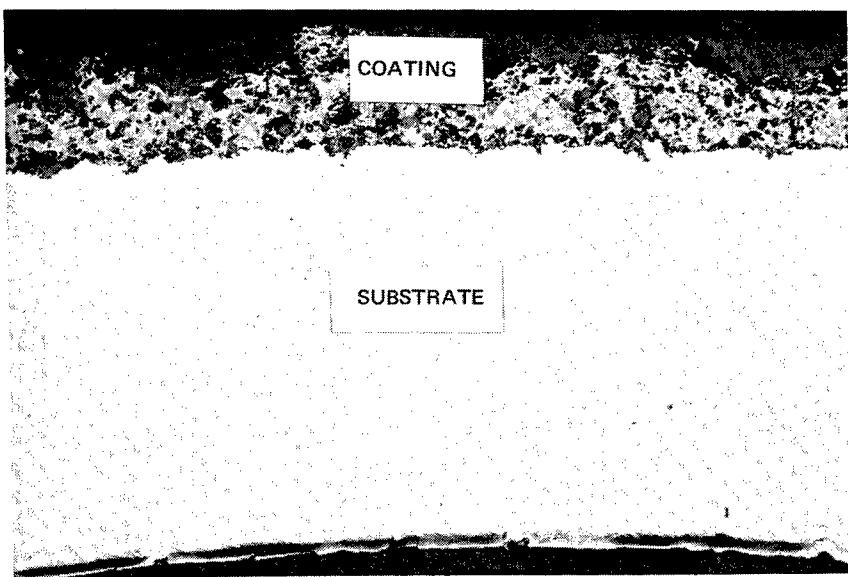
Mag: 200X

Figure 72   Unetched Photomicrograph of Columbium-1 Percent Zirconium Tube Coated With Iron Titanate and Cycled Between 1500° and 1800°F for 5,000 Hours

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Microhardness traverses were made on the cross section of the substrate, and the results are shown in Figure 73. The hardness after testing was higher than the hardness of the untested material, which was about 145 kg/mm^2. In addition, a significant hardness gradient extended from the outer surface to a depth of about 4 mils.
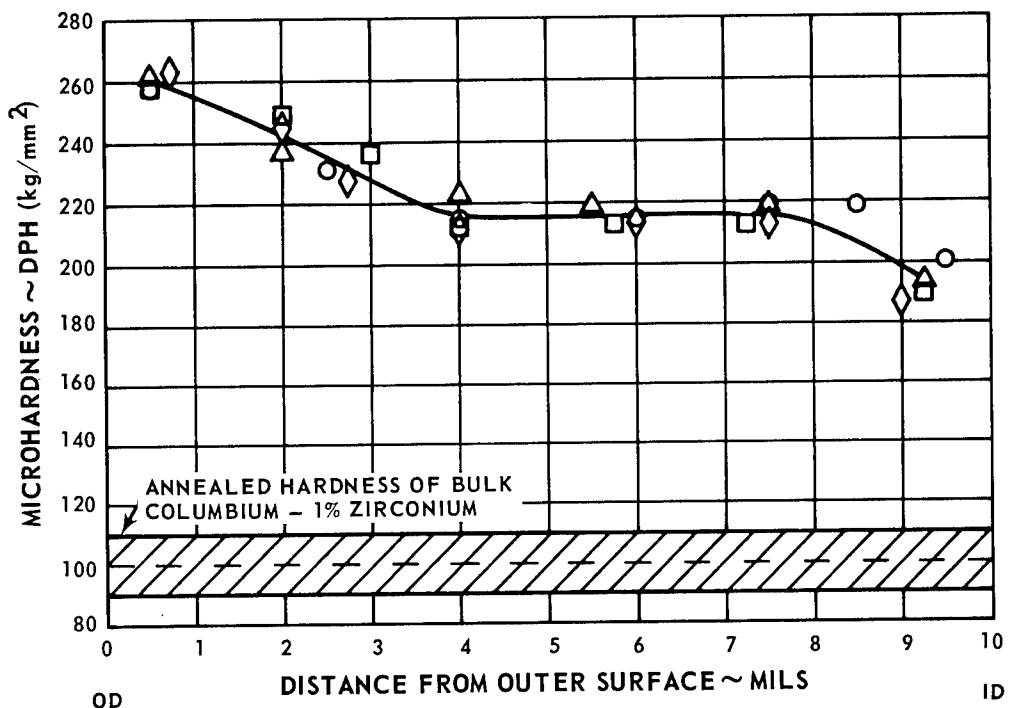
Figure 73   Microhardness Traverse of Columbium-1 Percent Zirconium Tube Coated With Iron Titanate and Thermally Cycled for 5,000 Hours Between 1500 and 1800°F

Electron microprobe analyses were conducted to determine if any diffusion of the coating elements occurred. Quantitative point count analyses for titanium and iron were made at the coating-substrate interface. The titanium concentration decreased from 0.08 weight percent at the surface to less than 0.01 weight percent at a depth of 1.5 mils, as shown in Table XXXII. The iron concentration decreased from 0.84 weight percent at the surface to less than 0.01 weight percent at a depth of 4.25 mils. The amount of iron and titanium diffusion is slightly less than that which occurred in the iron-titanate-coated columbium-1 percent zirconium specimen subjected to 10,000 hours of endurance testing.

TABLE XXXII

CONCENTRATIONS OF IRON AND TITANIUM ACROSS COLUMBIUM-1
PERCENT ZIRCONIUM TUBE COATED WITH IRON TITANATE AND
THERMALLY CYCLED BETWEEN 1500°F AND 1800°F FOR 5,000 HOURS

| Depth Below | Concentration (Weight Percent) | |
Interface (Mils)	Iron	Titanium
0.2	0.84	0.08
0.5	0.66	0.03
1.5	0.42	0
2.75	0.12	0
4.25	0	0

Note: Concentrations determined by electron beam microprobe analysis. Minimum detectable concentration for iron and titanium is 0.01 percent. Total wall thickness equals 10 mils.

X-ray line scans were made across the interface for titanium and columbium. These scans, shown in Figure 74, detected no significant interdiffusion of these elements.

Vacuum fusion oxygen analyses were performed on the columbium-1 percent zirconium substrate. The average oxygen content indicated by three full-section analyses was 0.42 weight percent, which is substantially higher than the oxygen content of untested material, which is 0.03 weight percent.

The hardness gradient and the overall increase in hardness of the substrate can be generally accounted for by the results obtained from the microprobe and vacuum fusion analyses. First, the solid solution hardening effects of iron and titanium were considered. One weight percent of iron increases the diamond pyramid hardness by 50 kg/mm^2 over the base hardness[4] and one weight percent of titanium increases the hardness by 40 kg/mm^2. From the known concentrations of iron and titanium in the substrate, the increases in hardness caused by solid solution hardening were calculated. The results are shown in Figure 75.
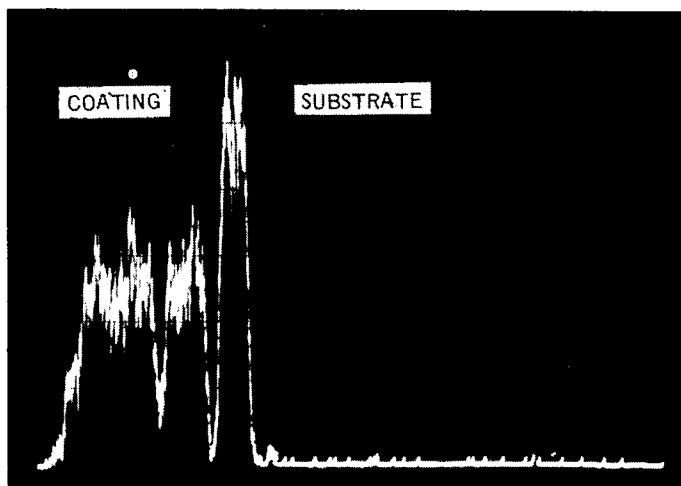
Relative Intensity
for Titanium
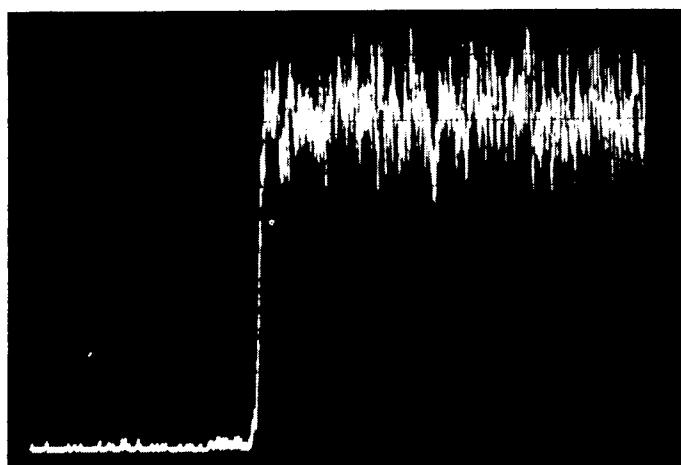
Relative Intensity
for Columbium
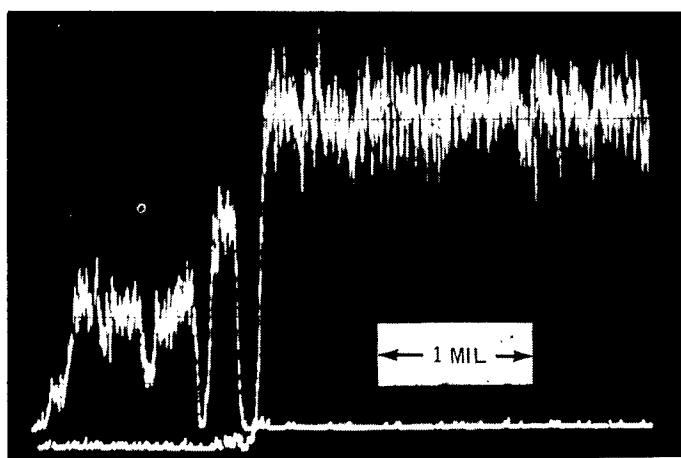
Composite Intensities for
Titanium and Columbium

Figure 74   X-ray Line Scan Intensities for Titanium and Columbium Across
Interface of Iron Titanate and Columbium-1 Percent Zirconium
After 5,000 Hours of Testing Between 1500°F and 1800°F

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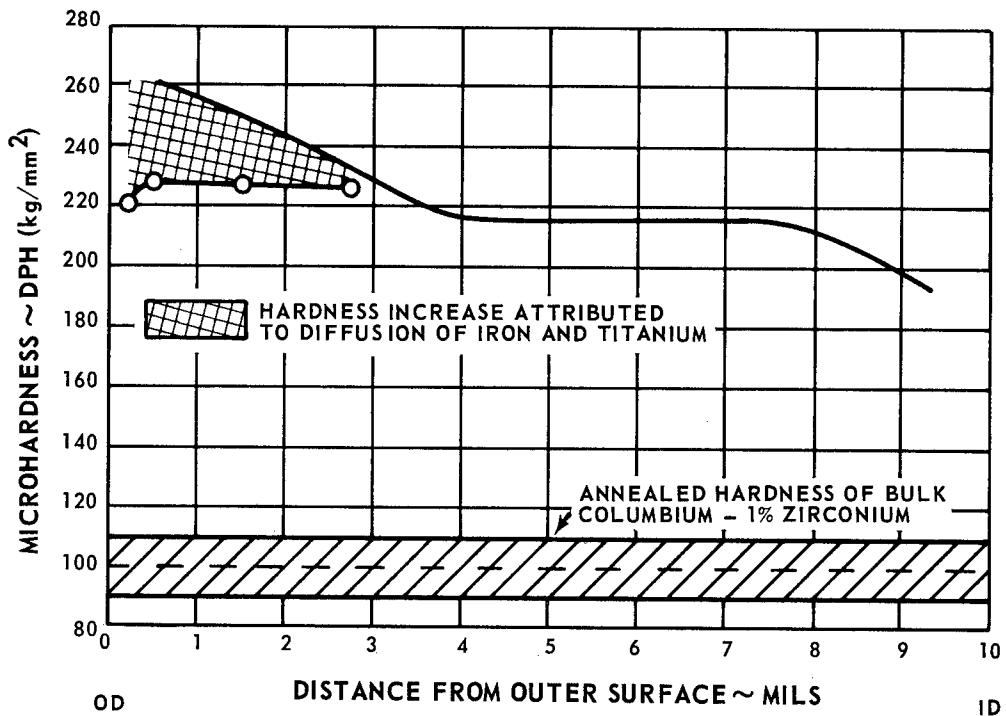
Figure 75   Effect of Iron and Titanium on Hardness of Columbium-1 Percent
Zirconium Tube Coated With Iron Titanate and Thermally Cycled
for 5,000 Hours Between 1500 and 1800°F

Excluding the gradient at the outer surface which is mostly accounted for by
iron and titanium diffusion, the hardness of the tested substrate is about 120
to 130 kg/mm^2 higher than it would be in the fully annealed condition. The
solid solution hardening effect of oxygen is 85 kg/mm^2 per 0.1 weight percent.[4]
Also, it has been calculated that the first 0.25 weight percent of oxygen which
enters the alloy would preferentially combine with zirconium and precipitate
as zirconium oxide particles. This precipitate has little effect on the room
temperature hardness of the alloy. Therefore, the total amount of oxygen
required to produce an increase in hardness of 120 to 130 kg/mm^2 is calculated
to be about 0.4 weight percent. The results of vacuum fusion oxygen analyses,
therefore, support the overall elevation in hardness which occurred as a result
of testing. Probable sources of oxygen, as reported earlier, are residual gases
in the test chamber, a thin oxide film formed on the inner surface during plasma-
arc spraying, and the iron-titanate coating. Data obtained from an aging test
independent of this contract of an uncoated columbium-1 percent zirconium tube
has verified that residual gases in the test chamber are a source of oxygen.
An uncoated tube identical to the one which was coated with iron titanate and
cycled for 5,000 hours was aged for 4,000 hours at 1700°F in a vacuum of 1 x
10^{-7} torr or better to obtain information on the oxygen pickup of the alloy which
results solely from the test environment. After aging, full-section vacuum fus-

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ion analyses detected 0.18 weight percent oxygen. Consequently, a significant portion of the oxygen detected in the substrate of the iron-titanate-coated specimen after the 5,000-hour cycling test came from residual gases in the test chamber. However, since the coated tube was cycled between 1500°F and 1800°F and the tests differed in duration, the exact amount of oxygen detected in the substrate of the coated tube attributable to residual gases cannot be calculated.

In summary, the iron-titanate-coated columbium-1 percent zirconium tube which was cycled 3,125 times from 1500°F to 1800°F in vacuum had a stable emittance of about 0.88 and demonstrated excellent coating-to-substrate adherence. Examination of the substrate after testing revealed that partial recrystallization had occurred. Also, an overall increase in hardness and a hardness gradient at the outer surface were detected. Limited diffusion of iron and titanium occurred across the coating-substrate interface. A significant amount of oxygen was detected in the substrate, and oxygen probably diffused across both the inner and outer surfaces. The hardness gradient at the outer surface and the overall increase in hardness were attributed to the solution hardening effects of iron, titanium, and oxygen.

2. Specimen Cycled Between 1500°F and 1900°F

The iron-titanate-coated columbium-1 percent zirconium tube which was cycled between 1500°F and 1900°F completed 10,058 hours of testing, During this period, the specimen was cycled 6291 times.

The emittance of the specimen (Figure 76) was about 0.89 at the start of the test, but after about 5,000 hours, the emittance decreased, reaching a value of about 0.77 at the end of the test. The decrease appeared to be associated with coating separation, since the specimen appeared mottled at elevated temperatures. The appearance of the specimen at 1500°F, 1700°F, and 1900°F at the end of the test is shown in Figure 77. After testing, no cracks could be positively identified in or near the test section, although cracks were found at some distance from the test section. One of these is shown in Figure 78. These cracks were probably produced when the tube ends were flattened for installation in the test rig. As shown in Figure 76, fluctuating vacuum readings were obtained during the last 4,000 hours of cyclic endurance testing. The reason for this behavior is not known.

The coating was subjected to X-ray diffraction and spectrographic analyses. The spectrographic analysis indicated that the concentrations of the more predominant impurities remained essentially unchanged during testing. The results of the spectrographic analyses are shown in Table XXXIII.
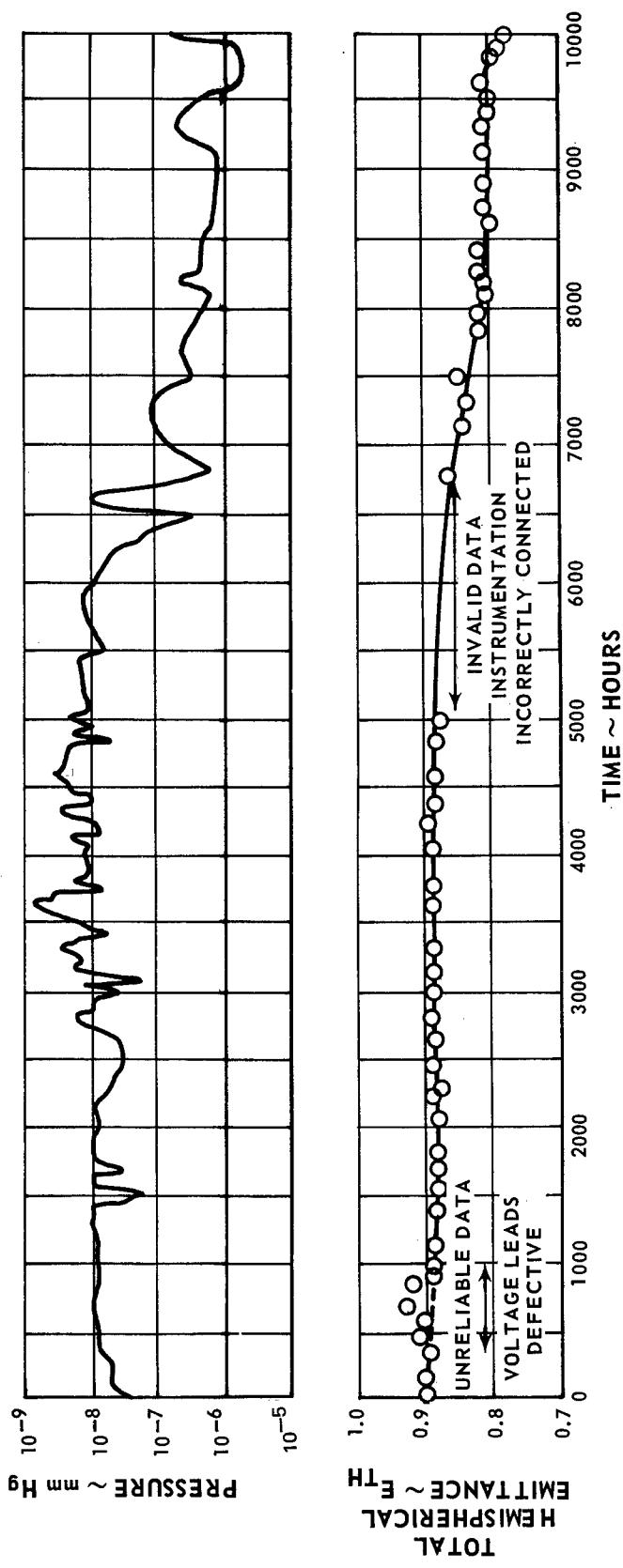
Figure 76   Pressure and Total Hemispherical Emittance for Iron–Titanate–Coated Columbium–1 Percent Zirconium Tube Cycled Between 1500°F and 1900°F

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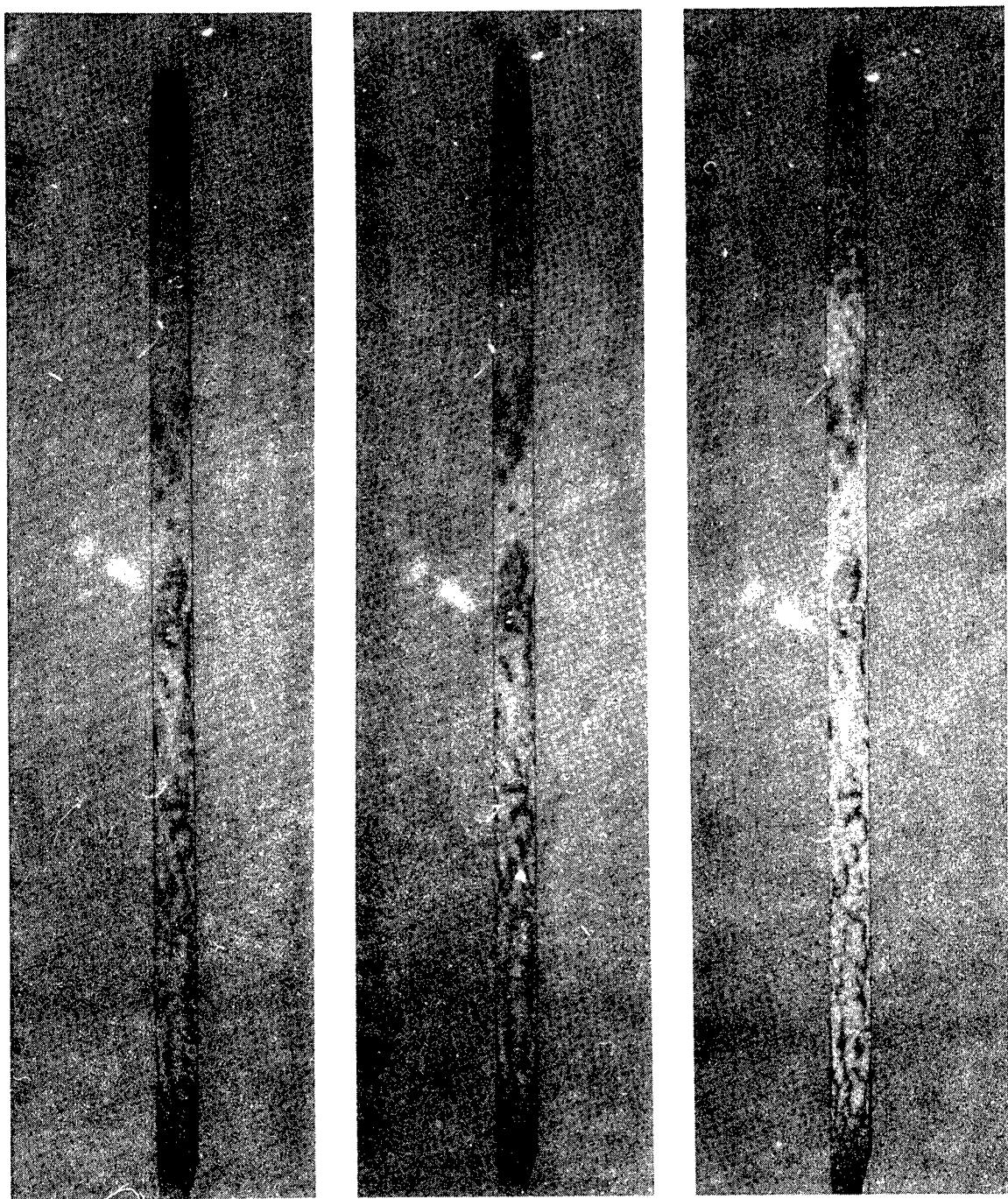
Figure 77   Iron-Titanate-Coated Columbium-1 Percent Zirconium Tube at
1500°F (Left), 1700°F (Center), and 1900°F (Right) in Vacuum
Prior to Completion of 10,000-Hour 1500°F to 1900°F Cycling Test

CN-11258/CN-11259/CN-11260
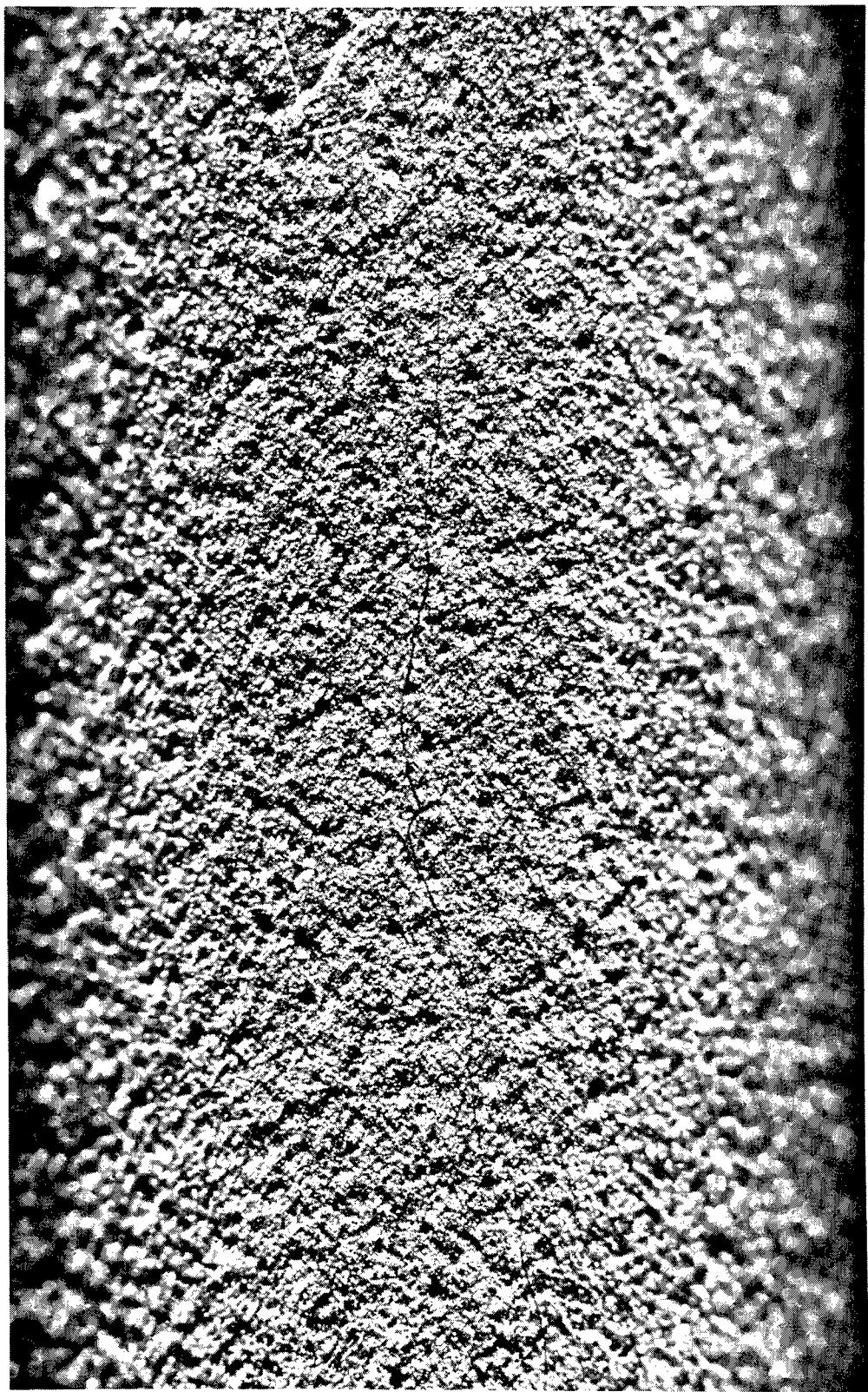
Mag: 20X

Figure 78   Close-up View of Surface of Iron–Titanate–Coated Columbium–1 Percent Zirconium Tube After
Thermal Cycling in Vacuum Between 1500°F and 1900°F for 10,000 Hours Showing Crack in
Coating Outside of Test Section

H–67962

TABLE XXXIII

RESULTS OF SEMIQUANTITATIVE SPECTROGRAPHIC
ANALYSIS OF IRON TITANATE ON COLUMBIUM-
1 PERCENT ZIRCONIUM WHICH WAS CYCLED
FOR 10,000 HOURS BETWEEN 1500°F AND 1900°F

	Impurity Content (Weight Percent)													
	Mn	Al	Mg	Si	Cb	Zn	Ca	Ag	Cr	Ni	Co	Cu	Sn	Mo	B
As Sprayed	0.4	0.5	0.2	0.4	–	–	–	–	0.2	–	–	trace	–	–	–
After Test	0.2	0.2	0.1	0.3	<0.1	<0.02	<0.1	trace	<0.03	trace	<0.01	–	0.01	<0.01	<0.01

X-ray diffraction analysis of the coating indicated that the major crystalline form present was iron titanate ($Fe_2(TiO_3)_3$). However, additional lines were present which are not associated with the $Fe_2(TiO_3)_3$ crystalline structure. It was not possible to relate these lines to a known crystalline structure at this time, but because of their high intensity, they should not be ignored. The results of the X-ray diffraction analysis are presented in Table XXXIV.

The substrate was sectioned and subjected to detailed analysis. When the substrate was sectioned, most of the coating in the center section spalled cleanly from the substrate, leaving no adherent particles. Hardness traces were made across the substrate at four locations near the center, and the results are shown in Figure 79. The hardness trends are generally in agreement with those obtained for the previously tested iron-titanate-coated columbium-1 percent zirconium specimens. The specimen was generally harder at the center of the tube where the temperature and emittance were measured than toward the ends where the material was cooler. At any axial location, the material near the outer wall was harder than that near the inner wall.

Metallographic examination of the substrate revealed a microstructure similar to that obtained previously with specimens tested for 5000 hours. The material was found to be partially recrystallized, as shown in Figure 80.

Analysis included a polishing and anodizing treatment in a solution containing 25 grams of oxalic acid, 25 grams of citric acid, 25 cubic centimeters of 85-percent phosphoric acid, 50 cubic centimeters of lactic acid, 175 cubic centimeters of water, and 300 cubic centimeters of ethyl alcohol. The specimen was anodized at 20 volts for less than one second. Subsequent metallographic examination showed yellow-stained phases scattered throughout the four mils near the inner wall of the tubing and a thin, sparse, discontinuous layer at the interface of the coating and the substrate (see Figure 81). Analysis indicated that this phase was most probably Cb_2C, although approximately 5 to 15 weight percent zirconium was also detected in the carbide regions.

TABLE XXXIV

X-RAY DIFFRACTION ANALYSIS RESULTS FOR IRON-TITANATE-COATED COLUMBIUM-1 PER CENT ZIRCONIUM TUBE AFTER BEING THERMALLY CYCLED BETWEEN 1500°F AND 1900°F FOR 10,000 HOURS

Line Number	Relative Intensity (Percent)	Spacing (Angstroms)	Spacing for $Fe_2(TiO_3)_3$ (Angstroms)
1	50	3.8287	
2	<10	3.6563	3.67
3	<10	3.4247	3.48
4	100	3.1605	
5	45	2.7049	2.68
6	40	2.5004	2.51
7	45	2.4470	2.47
8	<10	2.1952	2.19
9	10	2.1561	
10	10	1.8426	1.843
11	10	1.7114	1.68
12	100	1.6711	1.659
13	20	1.6116	1.626
14	20	1.4953	
15	<10	1.4730	1.477
16	20	1.4590	
17	<10	1.4477	
18	25	1.3789	1.358
19	<10	1.3383	1.339
20	<10	1.1500	
21	<10	1.1165	
22	<10	1.0911	
23	<10	1.0790	
24	<10	1.0715	
25	<10	1.0409	
26	<10	1.0346	
27	<10	1.0256	
28	<10	0.97090	
29	<10	0.96442	
30	<10	0.96094	
31	<10	0.92227	
32	<10	0.91990	
33	<10	0.91463	
34	15	0.90726	
35	<10	0.90512	
36	<10	0.90080	
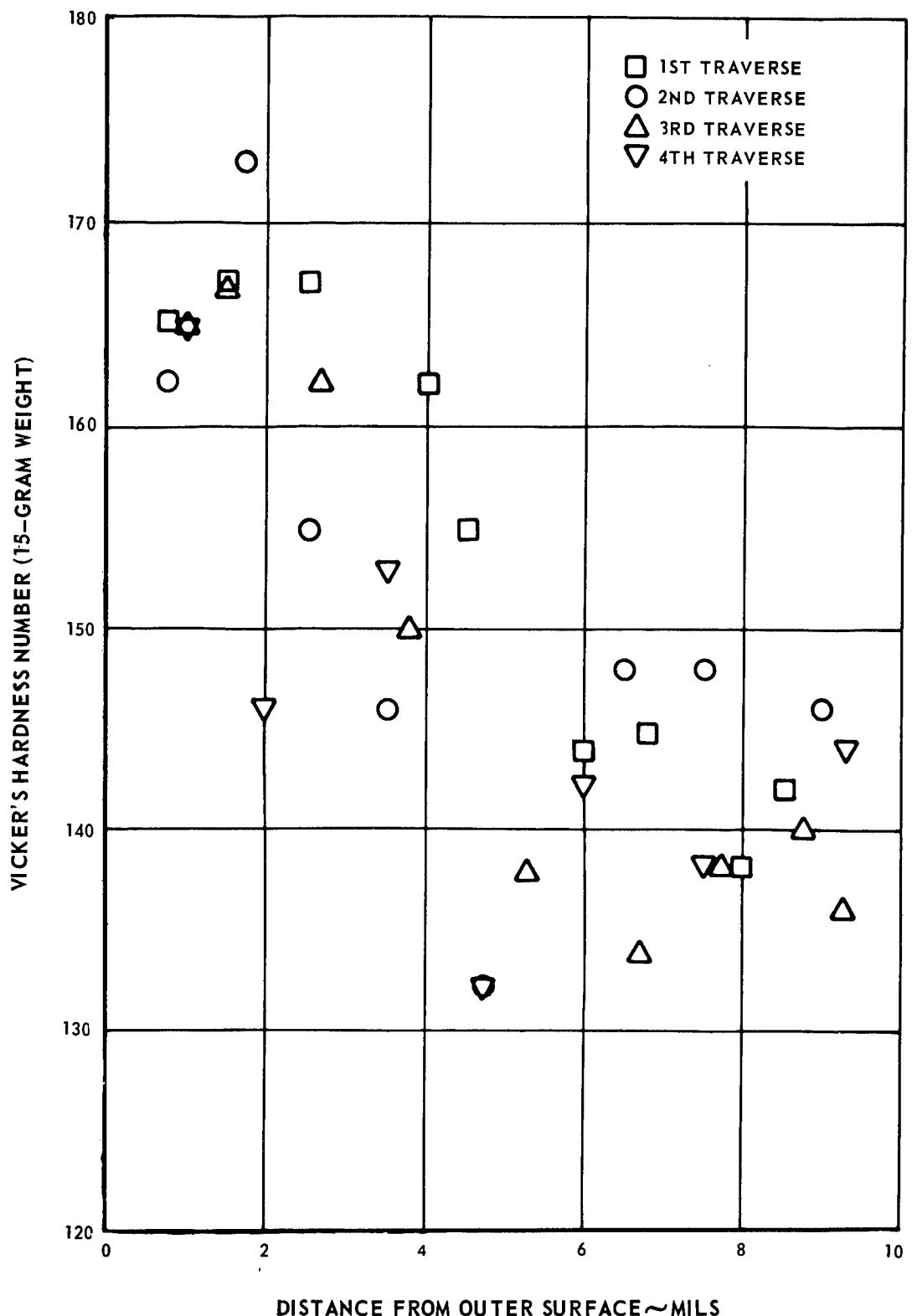
Figure 79   Hardness Traverse Test Results for Substrate of Iron-Titanate-
Coated Columbium-1 Percent Zirconium Tube After Cycling Between
1500°F and 1900°F for 10,000 Hours
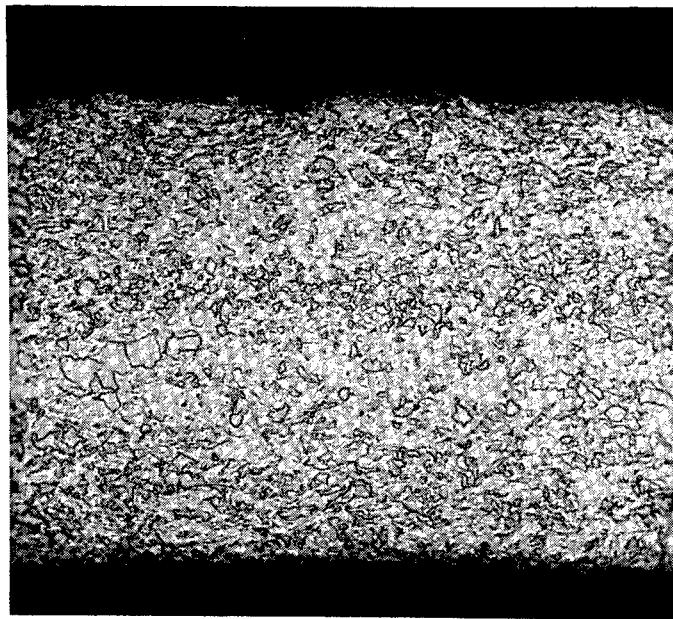
Mag: 250X

Etchant: 10% HF, 30% HNO₃, 60% H2O

Figure 80   Photomicrograph Showing Grain Structure of Columbium-1 Percent
             Zirconium Tube Coated With Iron Titanate and Cycled Between
             1500°F and 1900°F for 10,000 Hours
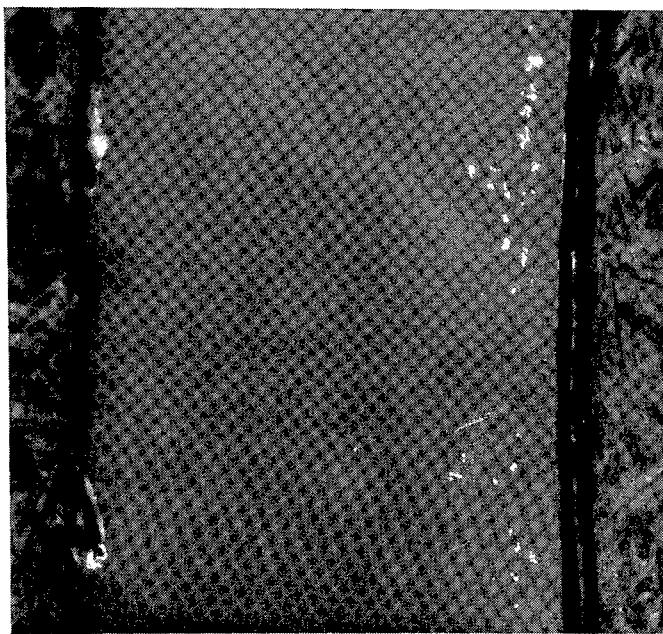
Mag: 250X

Polished and Anodized

Figure 81   Photomicrograph of Columbium-1 Percent Zirconium Tube Coated
             With Iron Titanate and Cycled Between 1500°F and 1900°F for 10,000
             Hours Showing Carbide Precipitates

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Microprobe analyses were performed across the substrate for iron, titanium, and zirconium. The zirconium concentration was generally uniform across the tube wall with an average value of 0.86 percent. Specifications for the substrate material specify a zirconium concentration between 0.8 and 1.2 percent. However, very fine oxide precipitates, rich in zirconium, were found dispersed throughout the tube, with a greater number being found near the outer tube wall. These oxides were observed since they visibly fluoresced under electron-beam bombardment. The microprobe analysis results for iron and titanium are shown in Figure 82. Gradients of both iron and titanium were found extending inward from the coating-substrate interface. The concentration of iron was about 0.74 weight percent at the interface and decreased to about 0.02 weight percent at a depth of 7.6 mils below the surface. The titanium concentration was about 0.09 weight percent at the interface and decreased to 0.01 weight percent at a depth of 5 mils below the surface.

Vacuum fusion analyses were performed for the complete substrate cross section for oxygen and carbon. The oxygen content was found to be 0.55 percent, and the carbon content was found to be 0.037 percent. The maximum specified levels for these constituents in the as-received columbium-1 percent zirconium are 0.03 percent oxygen and 0.01 percent carbon.

Comparison of the results for this specimen with those obtained for the other iron-titanate-coated columbium-1 percent zirconium specimens reveals several differences. The most significant of these is the lack of correlation between the substrate hardness and the measured concentrations of elements which diffused into the substrate. Aside from the effects of probe size, the hardness values obtained with the Vickers equipment for this specimen should have been approximately equal or slightly higher than the values obtained with the diamond pyramid hardness equipment used for the other iron-titanate-coated columbium-1 percent zirconium specimens. The slightly higher value would be expected in view of the comparable quantities of iron and titanium and the slightly higher oxygen content. However, the hardness level for this specimen was substantially lower than that observed for the other specimens. Apparently, the hardness is affected by constituents other than those for which analyses were performed. One possibility is nitrogen. Unfortunately, at the time that the last specimen was analyzed, the previously analyzed specimens were no longer available. Consequently, it was not possible to conduct additional tests to determine the cause of the apparent inconsistency.
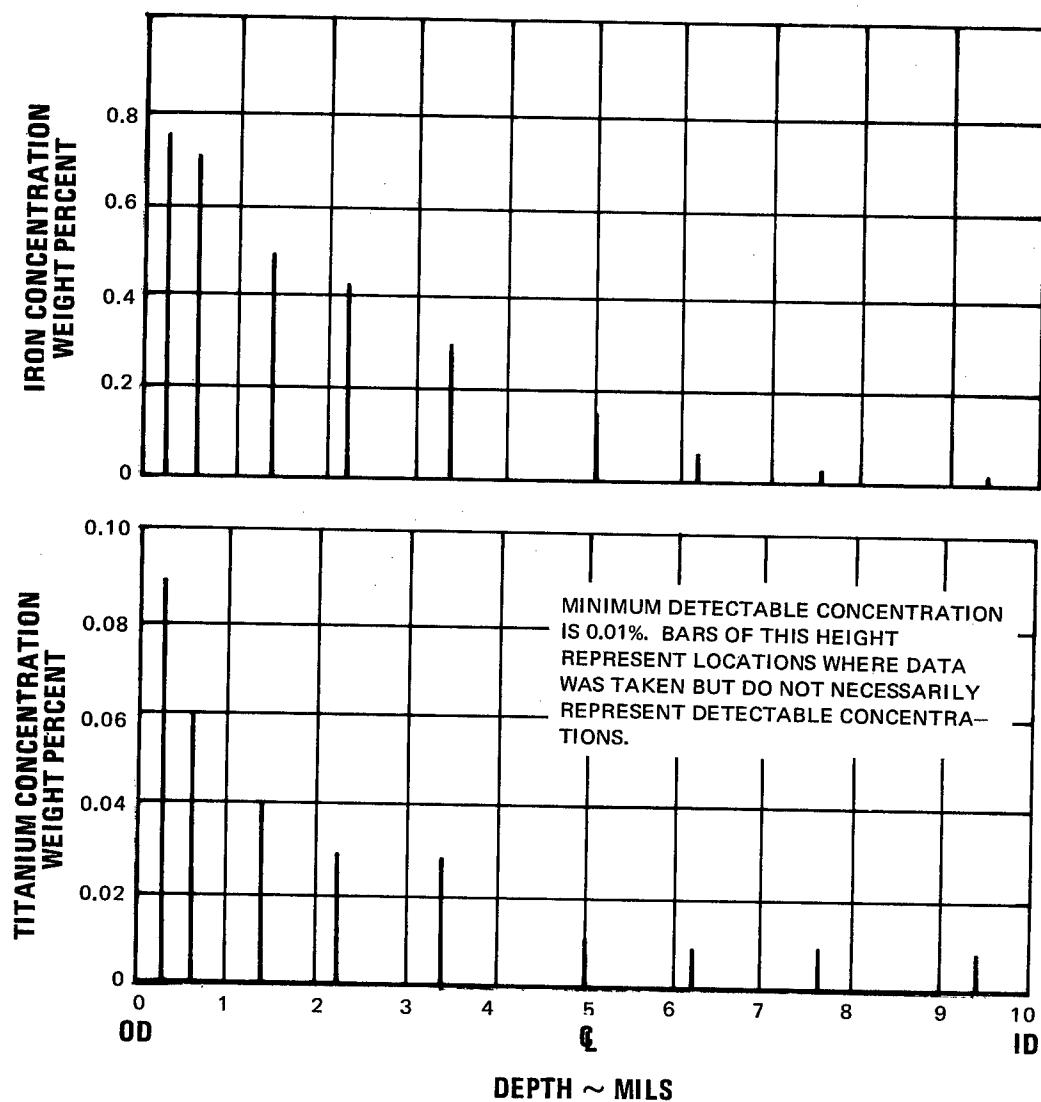
Figure 82   Concentrations of Iron and Titanium Across Columbium-1 Percent
Zirconium Tube Coated With Iron Titanate and Cycled Between
1500°F and 1900°F for 10,000 Hours

It is also not clear in what ways the coating behavior for this specimen differed
from that of the previously tested specimens other than the fact that coating se-
paration may have occurred at elevated temperatures, which had not been observed
previously.   The separation led to inspection of the coating for cracks, and, under
25-power magnification , cracks were found, but only near the crimped end of the
tube.   No cracks were positively identified in the test section.   The cracks which
were found outside the test section were not visible to the unaided eye.   It is
possible that similar cracks were present in previously tested specimens.

In summary, the 10,000-hour thermal cycling test of an iron-titanate-coated columbium-1 percent zirconium tube between 1500°F and 1900°F indicated that this test cycle results in coating separation and a general loss in emittance after about 5,000 hours of testing. The separation and the loss of emittance progressed as testing was continued. The deterioration of the performance of the specimen appears to be related only to the separation of the coating from the substrate. Changes occurring in the substrate were generally the same as those occurring in other columbium-1 percent zirconium tubes exposed to elevated temperature and vacuum for extended periods.

E. CONCLUSIONS

Thermal cycling of iron-titanate-coated columbium-1 percent zirconium specimens demonstrated that these materials are compatible and provide an emittance of about 0.88 when the maximum temperature is limited to 1800°F. Some changes in the coating structure occur and diffusion of coating constituents as well as oxygen into the substrate results in an increase in the substrate hardness above the fully annealed level, but these factors do not appear to affect the specimen emittance. Thermal cycling to 1900°F results in cracking and separation of the coating with an associated decrease in the specimen emittance.

PLASMA-ARC SPRAYING PROCEDURES

Substrate	Coating	Plasma Gas		Carrier Gas		Voltage (Volts)	Current (Amperes)
		Flow (cfh)	Pressure (psi)	Flow (cfh)	Pressure (psi)		
Beryllium	Calcium Titanante	78	50	50	50	32	600
	Iron Titanate	45	—	60	—	—	500
	Zirconium Titanate	72	14	60	2	30	350
Columbium – 1 Percent Zirconium	Aluminum Oxide Aluminum Titanate	45	—	45	—	30	600
	Barium Titanate	45	—	40	—	—	600
	Calcium Titanate	55	—	50	—	28	500
	Iron Titanate	65	13	60	3	28	500
	Stabilized Titanium Oxide	50	—	40	—	—	600
	Zirconium Diboride–Molybdenum Disilicide	42	—	25	—	—	725
	Zirconium Titanate	52	—	40	—	—	350
AISI-310 Stainless Steel	Calcium Titanate	52	—	40	—	30	500
	Iron Titanate	58	—	70	—	28	500

Note: Argon used for plasma gas and carrier gas for all coatings

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